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AN INVESTIGATION OF SOME DERIVATIVES OF ORTHOSULPHOBENZOIC ANHYDRIDE.[1]

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The investigations in this laboratory of the derivatives of orthosulphobenzoic acid, formed from the two isomeric chlorides of this acid, have shown many analogies and not less striking differences to the behavior of phthalic acid derivatives under similar conditions. It became, therefore, of interest to ascertain how the anhydride of orthosulphobenzoic acid would conduct itself toward reagents. To investigate this the present work was undertaken at the suggestion of Professor Remsen.

The anhydride of orthosulphobenzoic acid was prepared by Fahlberg and Barge,[2] by the action of acetyl chloride on the free acid; also by action of phosphorus pentachloride on the neutral potassium salt, the reaction being effected in a sealed tube, at 170°. They describe it as monoclinic crystals, melting at 119°.

About the same time Remsen and Dohme[3] obtained it by heating a mixture of the acid and phosphorus pentoxide at

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[1] From the author's dissertation, submitted to the Board of University Studies of the Johns Hopkins University for the degree of Doctor of Philosophy, June, 1896.

[2] Ber. d. chem. Ges., **22**, 754.

[3] This JOURNAL, **11**, 334.

130°, as a sublimate consisting of fine needles, melting at 128°.

Oscar Weber,[1] by the action of acetyl chloride, on metasulphoparatoluic acid, derived from "methyl saccharin," obtained its anhydride, and studied the action of ammonia upon it.

The anhydrides of various nitrosulphobenzoic acids have been obtained by workers in this laboratory.

The material used for the preparation of the anhydride in this work was the acid potassium salt of orthosulphobenzoic acid, obtained from commercial "saccharin" (containing about 60 per cent. benzoic sulphinide) by substantially the same method as described by Remsen and Saunders.[2]

The difficulties of handling and preserving the solutions in anhydrous ether or benzene led to the rejection of the methods of Fahlberg and Barge and of Weber. Sublimation did not yield the anhydride in sufficient quantity; moreover the crystals thus obtained, fine needles, decomposed much more rapidly than the large crystals obtained by the following

Method of Preparation.

The well-dried and powdered acid potassium salt (about 25 grams) is intimately mixed in a mortar, with the equivalent amount of phosphorus pentachloride (22 grams). The temperature at which the action begins varies with the purity of the chemicals. With pure, dry reagents it is difficult to induce action, but the presence of a small amount of phosphorus oxychloride considerably lowers the required temperature. After the evolution of hydrochloric acid has ceased, the mass is heated for some time to expel some of the oxychloride, and to melt the product which is then disintegrated on cooling, and placed in a continuous extractor and the separation effected by benzene. The supersaturated benzene solution in the extractor is allowed to cool very slowly and clear, colorless crystals, often 10 to 15 mm. in their longer diameter, and practically pure, are deposited.

The benzene employed must be pure; otherwise dark, sometimes blue, tarry products are obtained (an ethereal solution of the anhydride with some thiophene deposited a blue mass on exposure to the light). The presence of the phosphorus oxychloride in the solvent seems to favor the formation of better crystals.

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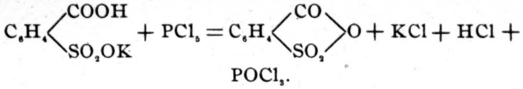
[1] Ber. d. chem. Ges., **22**, 1739.

[2] This JOURNAL, **17**, 347.

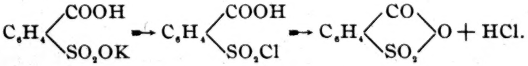
A simple and efficient extractor was prepared from ordinary laboratory apparatus. A test-tube 200 × 25 mm. was perforated with 20 or 30 holes, made by plunging a heated platinum wire through the glass. The mouth was then contracted to about 15 mm. in diameter, and several larger openings made near this end. In this the material to be extracted was placed, suspended by a platinum wire in a long-necked balloon-flask connected with an inverted condenser, and immersed in a water-bath, the single connection between flask and condenser being effected by means of a rubber stopper. The upper end of the condenser was provided with a calcium-chloride tube.

The reaction between the salt and pentachloride may be expressed:



$$C_6H_4\left\langle\begin{matrix}COOH\\SO_2OK\end{matrix}\right. + PCl_5 = C_6H_4\left\langle\begin{matrix}CO\\SO_2\end{matrix}\right\rangle O + KCl + HCl + POCl_3.$$

Limpricht and Uslar[1] have described a monochloride of metasulphobenzoic acid. It was thought that such a compound might be formed with the ortho acid, and break down with the formation of the anhydride, thus:



$$C_6H_4\left\langle\begin{matrix}COOH\\SO_2OK\end{matrix}\right. \rightarrow C_6H_4\left\langle\begin{matrix}COOH\\SO_2Cl\end{matrix}\right. \rightarrow C_6H_4\left\langle\begin{matrix}CO\\SO_2\end{matrix}\right\rangle O + HCl.$$

The reaction with pentachloride was brought about at a low temperature and the resulting mass poured into cold water. A bulky, flocculent precipitate separated which was washed with water until free from hydrochloric acid, and then dried between filter-paper. It seemed to have a definite melting-point and gave off hydrochloric acid when heated, and the residue was the anhydride. But, as the action of the pentachloride in sufficient proportion at low temperature seems to consist in the formation of the symmetrical dichloride, the reaction of the mass could be explained by assuming it to be a mixture of the anhydride and this chloride with some acid.

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[1] Ann. Chem. (Liebig), **106**, 30.

Different samples of the anhydride obtained by the described method were analyzed:

I. 0.1306 gram gave 0.2166 gram CO_2; 0.0300 gram H_2O.
II. 0.1567 gram gave 0.2611 gram CO_2; 0.0330 gram H_2O.
III. 0.1828 gram gave 0.3065 gram CO_2; 0.0389 gram H_2O.
IV. 0.2012 gram gave 0.2543 gram $BaSO_4$ (Liebig).

	Calculated for $C_7H_4SO_4$.	Found.			
		I.	II.	III.	IV.
C	45.64	45.23	45.44	45.58	....
H	2.17	2.56	2.34	2.36	....
S	17.39	....	....	....	17.39

The combustions were made with lead chromate mixture. Analysis I was made by Mr. E. S. Smith of this laboratory.

By the described method the anhydride is easily obtained in large, clear, colorless, monoclinic crystals, usually showing a prism and basal plane, sometimes a small orthopinacoid; cleavage prismatic.

The anhydride absorbs moisture quite rapidly if powdered or in small crystals, deliquescing to a sirup of orthosulphobenzoic acid. Large whole crystals are more stable, but become dull, and finally break down. It is soluble in anhydrous ether, benzene, or chloroform. Such solutions rapidly absorb moisture, and deposit crystals of orthosulphobenzoic acid. The melting-point of the pure anhydride is 129.5°. It sublimes apparently at or below its melting-point and can be distilled.

The anhydride may also be prepared in quantity by distilling the acid with phosphorus pentoxide.

Action with Alcohol.

Alcohols dissolve the anhydride with the formation of acid esters of orthosulphobenzoic acid. Similar esters were prepared by Remsen and Dohme[1] by the action of alcohols on the chloride. They ascribed the general formulæ given on account of the general properties and the ability to form chloroesters.

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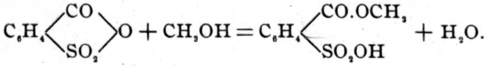
[1] This JOURNAL, 11, 341.

Methyl Alcohol.—When the anhydride is treated with methyl alcohol (absolute or 98 per cent.) it dissolves with evolution of heat. On evaporating the alcoholic solution a thick sirup is obtained, which slowly crystallizes in needles, exceedingly deliquescent and soluble ; they could not be obtained in any amount :

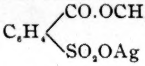


$$C_6H_4\left\langle\begin{matrix}CO\\SO_2\end{matrix}\right\rangle O + CH_3OH = C_6H_4\left\langle\begin{matrix}CO.OCH_3\\SO_2OH\end{matrix}\right. + H_2O.$$

The acid methyl ester has been described by Remsen and Dohme[1] and by Karslake.[2]

The *silver salt* was obtained by dissolving silver carbonate in the solution of the acid methyl ester. It crystallized from concentrated solution in methyl alcohol, in plates, the solution darkening considerably on exposure.

Of the crystals: 0.2005 gram gave 0.0663 gram metallic silver equivalent to 33.65 per cent. silver.



The formula $C_6H_4\left\langle\begin{matrix}CO.OCH_3\\SO_2OAg\end{matrix}\right.$ requires 33.4 per cent.

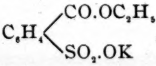
The *potassium salt* was similar to that described by Remsen and Dohme.

0.1480 gram gave 0.1422 gram $BaSO_4$ (Liebig method).

0.1638 gram gave 0.0563 gram K_2SO_4.

	Calculated for $C_7H_4SO_3.OC_2H_5.OK$.	Found.
S	12.59	12.51
K	15.39	15.50

Ethyl alcohol dissolves the anhydride easily, the alcoholic solution evaporating to a sirup, like the corresponding methyl compound, showing crystallization.



The *potassium salt*, $C_6H_4\left\langle\begin{matrix}CO.OC_2H_5\\SO_2.OK\end{matrix}\right.$, crystallizes in pearly plates and is very soluble.

0.2010 gram gave 0.0649 gram K_2SO_4, equivalent to 14.48 per cent. K ; above formula requires 14.58 per cent.

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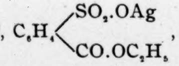
[1] This JOURNAL, **11**, 332.

[2] Dissertation J. H. U., 1895.

The *silver salt*,  $C_6H_4\begin{cases}SO_2.OAg\\CO.OC_2H_5\end{cases}$, crystallizes in deliquescent needles.

0.1243 gram gave 0.0395 gram silver equivalent to 31.76 per cent.

Action with Phenols.

By the action of phenols on the anhydride, sulphonphthaleïns were obtained in pure condition without difficulty. Some of these substances, especially the resorcinol derivatives, have been extensively studied in this laboratory.[1] By treating the free acid with phenols in presence of dehydrating agents, White obtained colored products, but not in any amount or in pure condition. Under the conditions employed by him the anhydride must have been present, and the failure to obtain better results can only be attributed to the temperatures employed.

The phthaleïns under certain conditions decompose on being heated, generally at about 150° with evolution of hydrogen sulphide. In this work it was found necessary to keep the temperature between 130° and 135°; below this, as a rule, the operation did not progress well; at higher temperatures decomposition often occurred, products being formed generally darker and less soluble than the sulphonphthaleïns, soluble in alkalies with only slight colors, not to be compared with those of the sulphonphthaleïns. These products were not further investigated.

The sulphonphthaleïns described were all produced by the direct action of the phenol and anhydride at temperatures between 130°–138°. The use of dehydrating agents was found to be unnecessary and objectionable, the yield being decreased by loss incurred in separating the dehydrating agent.

The following was the general method employed: The anhydride was mixed with somewhat more than twice the molecular equivalent of the phenol, in a porcelain crucible, and the mixture heated in an air-bath at 130°–135° for about twenty-four hours, with frequent stirring. The dark mass generally still had the odor of phenol, and showed green fluorescence. The mass was disintegrated with hot water, and boiled (until free from phenol or cresol), and concentrated so that most of the sulphonphthaleïn crystallized out on cooling. It was then filtered and washed with water; the filtration is slow and difficult and must be aided by suction. This generally furnished the phthaleïn in pure condition, but often it was necessary to dissolve in alkali and reprecipitate by acids. An amorphous powder was thus obtained exceedingly difficult to filter. The loss is considerable, most of the washing being done by decantation.

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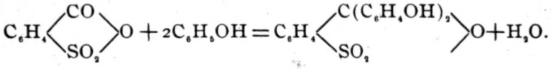
[1] This JOURNAL, **11**, 73; **14**, 455; **16**, 513, 528; **17**, 545, 556.

An attempt was made to induce combination at lower temperatures by treating solutions of the anhydride and phenols with dehydrating agents; but only with resorcinol was a slight color observed.

When the anhydride and phenol (or cresol) are mixed, a red color is seen, but the reaction does not seem to continue.

The filtrates from the sulphonphthaleïns were examined but no evidence of the formation of benzoylbenzenesulphonic acids could be found. The reaction takes place thus:



$$C_6H_4\left\langle\begin{matrix}CO\\SO_2\end{matrix}\right\rangle O + 2C_6H_5OH = C_6H_4\left\langle\begin{matrix}C(C_6H_4OH)_2\\SO_2\end{matrix}\right\rangle O + H_2O.$$

The sulphonphthaleins are intensely colored substances, more soluble in water than the corresponding derivatives of phthalic acid, and soluble in alcohol, from which they are precipitated in crystalline form by ether.

Varying the proportions did not alter the product, but only the rate of action and yield.

Phenolsulphonphthaleïn, $C_{19}H_{14}SO_5 = C\begin{cases}C_6H_4OH\\C_6H_4OH\\C_6H_4SO_2\\O\ —\end{cases}$ was obtained as a bright red crystalline powder, somewhat soluble in water, more so in alcohol, from which it was precipitated by ether as a yellowish-red crystalline powder, which on removal from the liquor instantly gave up ether, and solidified to a dark mass, which was apparently the same material.

The dilute alkaline solution is somewhat purer red than that of phenolphthaleïn; the more strongly alkaline solutions are purple. It is about as sensitive to alkalies and acids as phenolphthaleïn. The color does not disappear as readily on heating, and it might be used as an indicator with ammonia.

From the alkaline solution the sulphonphenolphthaleïn is precipitated as a dark red powder. By the slow cooling and evaporation of a solution in glacial acetic acid, the phenolsulphonphthaleïn was obtained in distinct nodules of radiating needles, blue-green by reflected, and deep-red by transmitted light. On analysis the following results were obtained:

I. 0.2144 gram gave 0.5063 gram CO_2; 0.0876 gram H_2O.
II. 0.1669 gram gave 0.3656 gram CO_2, 0.0666 gram H_2O.
III. 0.2254 gram gave 0.1456 gram $BaSO_4$.
IV. 0.2247 gram lost 0.0028 gram at 135° = 1.23 per cent.

	Calculated for $C_{19}H_{14}SO_5$.	Found. I.	II.	III.
C	64.40	64.35	64.20	....
H	3.90	4.53	4.43	....
S	9.04	....	....	8.84

Phenolsulphonphthaline.—The alkaline solution of the sulphonphthaleïn was treated with zinc dust; the yellowish solution was filtered in an atmosphere of hydrogen, when, after the removal of the zinc, and most of the potassium salts, small granular crystals were formed, probably of the leuco base, dihydroxytriphenylmethanesulphonic acid.

Dibromphenolsulphonphthaleïn, $C_{19}H_{12}Br_2SO_5$. — Phenolsulphonphthaleïn, in glacial acetic acid, was treated with excess of bromine dissolved in glacial acetic acid; the acid was rapidly expelled by a current of air, and the bromine derivative deposited as a granular, purplish, crystalline powder.

0.2050 gram gave 0.0871 gram silver and 0.0983 gram $BaSO_4$ (Carius' method), equivalent to 31.47 per cent. bromine and 6.37 per cent. sulphur. $C_{19}H_{12}Br_2SO_5$ requires 31.25 per cent. bromine and 6.27 per cent. sulphur.

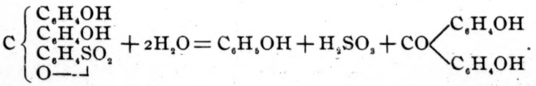
Dibromphenolsulphonphthaleïn gives a blue to purple color with alkalies. This color disappears on standing with excess of alkali, with formation of a green fluorescent solution. The acid solution is yellow. It is extremely delicate as an indicator, is sensitive to ammonia, not sensitive to carbon dioxide, gives a decided blue color with tap water (hardness about 3°).

An effort was made to prepare an acetyl derivative by boiling the phenolsulphonphthaleïn with acetic anhydride, but apparently none was formed; anhydrous ether added to the solution separated the peculiar precipitate above mentioned, which seemed to be the same substance.

Phenolsulphonphthaleïn was heated in a sealed tube with concentrated hydrochloric acid for five hours at 170°–180°, but no action could be detected. On heating for two hours at 230°–240° decomposition was effected. Considerable pressure was observed on opening the tube; the liquid portion yielded only phenol and sulphur acids; the black solid residue yielded only a slight color to alkali, and was apparently carbon, yielding nothing on distillation.

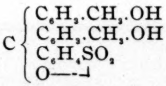
In order to obtain a dihydroxytriphenylmethanesulphonic acid, the sulphonphthaleïn was boiled for fifty hours with hydrochloric acid, but no indication of such decomposition could be detected in the result. Boiling for fifty hours with excess of barium hydroxide also failed to produce any change. With dilute potassium hydroxide no action could be detected on boiling for a week; with concentrated caustic potash decomposition was effected in several hours, but the products could not be separated from the excess of alkali.

On heating the phenolsulphonphthaleïn in melted caustic potash the mass was found to contain sulphite, phenol, and a crystallizable substance identified as paradihydroxybenzophenone, as described by Baeyer and Burkhardt.[1]



$$C\left\{\begin{array}{l} C_6H_4OH \\ C_6H_4OH \\ C_6H_4SO_2 \\ O\text{—}\lrcorner \end{array}\right. + 2H_2O = C_6H_5OH + H_2SO_3 + CO\left\langle\begin{array}{l} C_6H_4OH \\ C_6H_4OH \end{array}\right. .$$

Orthocresolsulphonphthaleïn, $C_{21}H_{18}SO_5 = $



$$C\left\{\begin{array}{l} C_6H_3.CH_3.OH \\ C_6H_3.CH_3.OH \\ C_6H_4SO_2 \\ O\text{—}\lrcorner \end{array}\right.$$

was obtained by the same method as the phenolphthaleïn. It crystallized from water, more easily than its lower homologue, appearing beetle-green by reflected and deep carmine by transmitted light. It is less soluble in water than the phenol compound, and the alkaline solutions are purple to carmine according to dilution, the neutral or dilute acid yellow, with strong acids, salmon color.

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[1] Ann. Chem. (Liebig), **202**, 196.

On analysis the following figures were obtained :

I. 0.1731 gram gave 0.4182 gram CO_2 ; 0.0755 gram H_2O.
II. 0.1558 gram gave 0.3762 gram CO_2 ; 0.0694 gram H_2O.
III. 0.2016 gram gave 0.1240 gram $BaSO_4$ (Liebig method).

	Calculated for $C_{21}H_{18}SO_5$.	Found. I.	II.	III.
C	65.99	65.90	65.85	....
H	4.71	4.85	4.95	....
S	8.37	....	....	8.45

Dibromorthocresolsulphonphthaleïn, $C_{21}H_{16}Br_2SO_5$, was obtained by treating the acetic acid solution with bromine; it resembles the phenol compound in color and general properties.

The analysis gave the following results :

I. 0.2051 gram gave 0.0804 gram Ag, and 0.0866 gram $BaSO_4$.

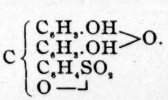
II. 0.2280 gram gave 0.0900 gram Ag, and 0.0962 gram $BaSO_4$.

	Calculated for $C_{21}H_{16}Br_2O_5$.	Found. I.	II.
Br	29.26	29.10	29.05
S	5.95	5.79	5.83

On boiling the orthocresolsulphonphthaleïn with acetic anhydride it lost most of its color, nor did the alkaline solution show the intense color immediately. The acetyl derivative appeared to be easily saponifiable, and was not isolated.

Paracresolsulphonphthaleïn was much more difficult to prepare than the ortho compound ; it was not obtained pure. It had a yellow color somewhat fluorescent.

Resorcinolsulphonphthaleïn, $C_{19}H_{12}SO_6$ =



$$C\begin{cases} C_6H_3.OH \\ C_6H_3.OH \\ C_6H_4SO_2 \\ O\text{—┘} \end{cases}\!\!>O.$$

This substance could be produced much more easily and at lower temperature than the phenol derivatives. As shown by previous workers in this laboratory, resorcinol forms various condensation-products, all intensely colored fluorescent substances. It is worthy of note, however, that while Remsen and Linn[1] and Blackshear[2] produced only the diresorcinol derivative from the dioxybenzoylbenzenesulphonic acid, Remsen and McKee[3] produced the same substance from the chlorides, at low temperatures; at higher temperatures different derivatives are obtained.

In this work the materials were maintained at as low a temperature as possible to maintain action. The sulphonphthaleïn was obtained as a bright reddish-yellow powder, intensely fluorescent in alkaline solution. The color is more red than that of fluoresceïn, and is more quickly destroyed by excess of alkali. The bromine derivative is not as intense in color as eosin. Sulphonfluoresceïns have been described in detail by Remsen and Linn, and Blackshear.

Of the phthaleïn:

I. 0.1358 gram gave 0.3060 gram CO_2, and 0.0450 gram H_2O.

II. 0.2214 gram gave 0.1320 gram $BaSO_4$.

	Calculated for $C_{19}H_{12}SO_6$.	Found.
C	61.90	61.44
H	3.26	3.71
S	8.69	8.18

III. 0.3100 gram lost 0.0140 gram on heating at 135° for four hours, equivalent to 4.54 per cent.

IV. Dried in a desiccator, over sulphuric acid, 0.2024 gram lost 0.0057 gram at 130°, equivalent to 2.81 per cent.; residue gave 0.0846 gram $BaSO_4$ (Liebig) equivalent to 5.73 per cent. sulphur.

V. Dried in air (eight weeks), 0.2043 gram lost 0.0094 gram at 135°, equivalent to 4.65 per cent.; residue gave 0.0868 gram $BaSO_4$ (Liebig) equivalent to 5.82 per cent. sulphur. The odor of hydrogen sulphide was noticeable in the air-bath.

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[1] This JOURNAL, **11**, 73.

[2] *Ibid*, **14**, 455.

[3] *Ibid*, **18**, 798.

Orcinolsulphonphthaleïn was formed easily and cleanly. It was not analyzed. It has been described in detail by Gilpin.[1]

Hydroquinolsulphonphthaleïn.—Hydroquinol reacted more slowly than resorcinol, and the mass as obtained by precipitation of the alkaline solution by acid, was dark brown and exceedingly difficult to filter. It is less soluble than the sulphonfluoresceïn, the alkaline solution being brown-yellow and not fluorescent.

I. 0.1930 gram gave 0.0158 gram $BaSO_4$, equivalent to 8.15 per cent. sulphur.

II. 0.1544 gram gave 0.0125 gram $BaSO_4$, equivalent to 8.04 per cent. sulphur.

The formula $C_{19}H_{14}SO_8$ requires 8.26 per cent. sulphur.

Pyrogallolsulphonphthaleïn (*Sulphongalleïn*), $C_{19}H_{10}O_8S$.—Pyrogallol reacts easily with the anhydride; the green product was disintegrated with much hot water, and purified by washing with water, and thus obtained as a blue-brown powder, somewhat soluble, giving a yellow to red color with acids, and an intense blue with alkalies, which rapidly became purple on exposure to the air, finally becoming a dirty green and brown, and depositing a brown precipitate. The addition of some stannous chloride to the alkaline solution preserves it for some time.

I. 0.2112 gram gave 0.1215 gram $BaSO_4$.

II. 0.2075 gram gave 0.1185 gram $BaSO_4$.

III. 0.1702 gram gave 0.3565 gram CO_2, and 0.040 gram H_2O.

	Calculated for $C_{19}H_{10}O_8S$.	Found. I.	 II.	 III.
C	57.28	....	....	57.12
H	2.51	....	....	2.60
S	8.14	7.89	7.84	....

An attempt to prepare the phthaline was unsuccessful, decomposition resulting.

m-Amidosulphonphthaleïn, $C_{19}H_{14}N_2O_4S$, was obtained as a reddish-brown powder, soluble in alkalies. These solutions are yellow, with a green fluorescence, by no means as strong as that of the sulphonfluoresceïn. Treatment with acetic anhydride failed to yield any derivative.

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[1] This JOURNAL, **16**, 528.

0.2379 gram gave 0.210 gram $BaSO_4$, equivalent to 8.82 per cent. sulphur.

Formula $C_{19}H_{14}N_2O_4S$ requires 8.74 per cent. sulphur.

p-Amidophenolsulphonphthaleïn isomeric with the above compound was obtained, impure, as a dark mass, more soluble than the sulphonrhodamine. It gave an intense blue-green with alkalies, red with acids, and is easily destroyed by oxidation in alkaline solution.

Salicylic acid melted with the anhydride yielded a bright-red coloring-matter.

Action with Ammonia.

The action of ammonia on the anhydride of orthosulphobenzoic acid has been studied by Fahlberg and Barge and verified in the present work. Weber studied the action of ammonia on the anhydride of metasulphoparatoluic acid, and in both cases the result was the formation of the ammonia salt of the benzamine acid.

The anhydride was dissolved in anhydrous ether (or benzene) and dry ammonia gas passed into the solution with continual shaking, until thoroughly saturated. A white crystalline precipitate was formed; this was filtered off thoroughly and washed with anhydrous ether. Nothing was obtained from the ether but a little anhydride unacted upon.

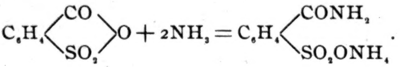
The white substance was very soluble in water, from which it crystallized in nodules, and in alcohol from which it crystallized in needles; it is less soluble in absolute alcohol. It did not taste sweet, nor did it become sweet on heating, as sulphaminebenzoic acid does. In some cases a *faint* sweet taste was detected. It melted sharply at 256°–257°.

On analysis:

I. 0.2160 gram gave 0.0274 gram N (Kjeldahl).
II. 0.2511 gram gave 0.0151 gram N (by KOH).
III. 0.1531 gram gave 0.1638 gram $BaSO_4$.
IV. 0.1421 gram gave 0.1528 gram $BaSO_4$.
V. 0.1326 gram gave 0.1388 gram $BaSO_4$.

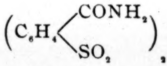
	Calculated for $C_7H_{10}SN_2O_4$.	Found. I.	II.	III.	IV.	V.
N_2	12.88	12.67	....	....	....	....
S	14.67	....	....	14.70	14.75	14.65
N by KOH	6.44	....	6.39	....	....	....

Determination V. was by Mr. E. E. Reid, of this laboratory. The reaction of the anhydride and ammonia may be represented :



$$C_6H_4\langle{}^{CO}_{SO_2}\rangle O + 2NH_3 = C_6H_4\langle{}^{CONH_2}_{SO_2ONH_4}.$$

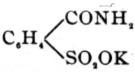
The result being the ammonium salt of benzaminesulphonic acid.

Barium benzaminesulphonate,  $\left(C_6H_4\langle{}^{CONH_2}_{SO_2}\right)_2$ Ba.5H$_2$O, was obtained from the ammonium salt. It is very soluble in water, the solution evaporating to a thick syrup, and finally to a glass. From dilute alcohol it crystallized in white tufts or brittle needles. The same salt has been derived from cyanbenzenesulphonic acid described by Remsen and Karslake.[1]

I. 0.4360 gram lost 0.0627 gram at 140°, and gave 0.1625 gram $BaSO_4$.

II. 0.3532 gram lost 0.0513 gram at 140°, and gave 0.1316 gram $BaSO_4$.

	Calculated for $(C_7H_6NSO_4)_2Ba.5H_2O$.	Found. I.	II.
H_2O	14.35	14.15	14.52
Ba	21.85	22.05	21.92

Potassium benzaminesulphonate,  $C_6H_4\langle{}^{CONH_2}_{SO_2OK}$.H$_2$O, crystallized from dilute alcohol in small needles, easily soluble in water.

I. 0.2318 gram lost 0.0159 gram at 140° and gave 0.0784 gram K_2SO_4.

II. 0.1813 gram lost 0.0129 gram at 140° and gave 0.0633 gram K_2SO_4.

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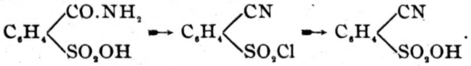
[1] This JOURNAL, 18, 826.

	Calculated for $C_7H_6SO_4NK.H_2O$.	Found.	
		I.	II.
H_2O	7.00	6.88	7.11
K	15.21	15.22	15.26

The potassium salt was treated with phosphorus pentachloride; the oily chloride thus obtained was decomposed by boiling with water, neutralized by ammonia, and crystallized in botryoidal crystals characteristic of the orthocyanbenzenesulphonic acid.



$$C_6H_4{<}\begin{matrix}CO.NH_2\\SO_2OH\end{matrix} \rightarrow C_6H_4{<}\begin{matrix}CN\\SO_2Cl\end{matrix} \rightarrow C_6H_4{<}\begin{matrix}CN\\SO_2OH\end{matrix}.$$

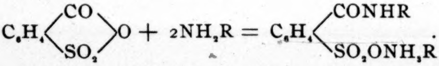
The barium benzaminesulphonate was titrated with sulphuric acid, filtered, and evaporated to a sirup; no crystals could be obtained. Fahlberg and Barge describe it as crystallizing in needles. Neither Jesurun[1] nor Remsen and Karslake[2] could obtain it in crystals.

Action with Aromatic Amides.

With aniline and toluidines the action was analogous to that with ammonia. The anhydride and base, dissolved in anhydrous benzene or ether, were mixed, when a pasty colorless mass separated. When equimolecular quantities were used, addition of more base produced further precipitation until a second equivalent of base had been added. The mass suspended in benzene, on long boiling, usually became hard and somewhat crystalline. It was well washed with benzene, and on treatment with water dissolved entirely.

By mixing the base and anhydride and heating, the same substances resulted, but they were usually darker and more difficult to purify.

On examination these substances proved to be the salt of the base with a benzanilido acid.



$$C_6H_4{<}\begin{matrix}CO\\SO_2\end{matrix}{>}O + 2NH_2R = C_6H_4{<}\begin{matrix}CONHR\\SO_2ONH_3R\end{matrix}.$$

The general properties of the acids are the same. The acids are very soluble, none being obtained in crystallized state, in marked distinction to the isomeric sulphanilido acids. The salts crystallize slowly from concentrated solution; often they separate as an oil, which becomes crystalline only on very long standing, and some also become liquid before dissolving.

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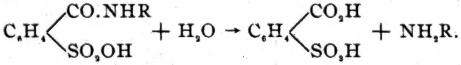
[1] Ber. d. chem. Ges., **26**, 2288.

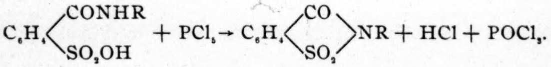
[2] *Loc. cit.*

In neutral solution they are generally stable, but often become discolored in the light. They are decomposed by long boiling with acids or strong alkali, with separation of the base, and formation of orthosulphobenzoic acid.



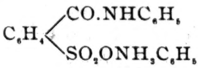
$$C_6H_4\begin{cases}CO.NHR\\SO_2OH\end{cases} + H_2O \rightarrow C_6H_4\begin{cases}CO_2H\\SO_3H\end{cases} + NH_2R.$$

With phosphorus pentachloride the corresponding sulphinide derivative is formed:



$$C_6H_4\begin{cases}CONHR\\SO_2OH\end{cases} + PCl_5 \rightarrow C_6H_4\begin{cases}CO\\SO_2\end{cases}NR + HCl + POCl_3.$$

These have been described by Remsen and Coates,[1] and by Remsen and Kohler, and are decomposed on boiling with alkali, with formation of sulphanilido compounds, which are less soluble and well crystallized.

Aniline Benzanilidosulphonate,  $C_6H_4\begin{cases}CO.NHC_6H_5\\SO_2ONH_3C_6H_5\end{cases}$, was the only product obtained by the action of aniline on the anhydride. The mass as obtained was exceedingly soluble in water and in alcohol; insoluble in benzene and ether. On direct evaporation of the concentrated solution an oil or paste was obtained, which would not crystallize, and darkened on exposure to light and air. On slow evaporation of a solution in dilute alcohol *in vacuo*, or better over sulphuric acid, white tufts of radiating needles were obtained. These gave the reactions for aniline, and were very soluble and difficult to crystallize. They did not lose weight on heating to 140°, but began to turn dark green.

I. 0.2056 gram gave 0.1276 gram $BaSO_4$ (Carius method).
II. 0.1851 gram gave 0.1144 gram $BaSO_4$ (Carius method).
III. 0.2621 gram gave 0.0203 gram N (Kjeldahl).

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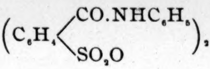
[1] This JOURNAL, **17**, 311, et seq.

	Calculated.	I.	II.	III.
S	8.64	8.52	8.49	....
N	7.84	....	....	7.75

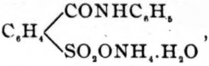


Barium Benzanilidosulphonate $\left(C_6H_4\left\langle\begin{matrix}CO.NHC_6H_5\\SO_2O\end{matrix}\right.\right)_2Ba.5H_2O$, is very soluble in water, and could not be crystallized from it. The solution evaporated to a hard transparent glass. From dilute alcohol it crystallized in fine, radiating, chalky needles. It is very soluble in water although the crystals dissolve but slowly.

I. 0.2211 gram lost 0.0258 gram and gave 0.0658 gram $BaSO_4$.

II. 0.2131 gram lost 0.0262 gram and gave 0.0638 gram $BaSO_4$.

	Calculated for $(C_{13}H_{10}NO_4S)_2Ba.5H_2O$.	Found. I.	Found. II.
Ba	17.38	17.51	17.61
H_2O	11.55	11.67	11.81

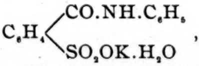


Ammonium Benzanilidosulphonate, $C_6H_4\left\langle\begin{matrix}CONHC_6H_5\\SO_2ONH_4.H_2O\end{matrix}\right.$, is very soluble in water, and crystallized quite readily in silky, radiating needles.

I. 0.2112 gram gave 0.0106 gram NH_3.

II. 0.2326 gram lost 0.0133 gram at 130°, and gave 0.1745 gram $BaSO_4$.

	Calculated for $C_{13}H_{14}N_2SO_4.H_2O$.	Found. I.	Found. II.
H_2O	5.76	....	5.75
S	10.25	....	10.27
NH_3	5.45	5.50	....



Potassium Benzanilidosulphonate, $C_6H_4\left\langle\begin{matrix}CO.NH.C_6H_5\\SO_2OK.H_2O\end{matrix}\right.$, slowly separated from dilute alcoholic solution in fine silky crystals.

I. 0.2762 gram lost 0.0165 gram at 130°, gave 0.0691 gram K_2SO_4.

II. 0.2516 gram lost 0.0139 gram at 140°, gave 0.0651 gram K_2SO_4.

	Calculated.	I.	II.
H_2O	6.00	5.94	5.52
K	11.73	11.22	11.50

The *cadmium* salt separated as a poorly crystalline powder.

I. 0.2920 gram gave 0.2015 gram $BaSO_4$.

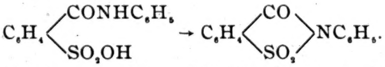
II. 0.2265 gram gave 0.0398 gram CdO.

	Calculated.	Found.
Cd	16.83	16.70
S	9.63	9.48

The *sodium*, *copper* and *lead* salts evaporated to hard glasses, and the *silver* salt decomposed on evaporation.

The *free acid* was obtained from the lead salt (by hydrogen sulphide) as a thick sirup; neither water nor alcoholic solution showed any sign of crystallization within three months.

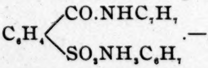
Action of Phosphorus Pentachloride.—The potassium salt was treated with phosphorus pentachloride; on adding water a white solid separated. This was washed with water and proved to be free from chlorine. It crystallized from alcohol in flat needles; on recrystallization from ether it melted sharply at 190°–191° (uncorr.). It was insoluble in acid, and in cold alkali; dissolved by boiling alkali and precipitated by acids. This, crystallized from hot water, had the melting-point 159° (uncorr.); corresponding to the anil and sulphanilido acid, the action of the pentachloride being therefore one of dehydration:



$$C_6H_4\left<\begin{matrix}CONHC_6H_5\\SO_2OH\end{matrix}\right. \rightarrow C_6H_4\left<\begin{matrix}CO\\SO_2\end{matrix}\right>NC_6H_5.$$

Equimolecular quantities of aniline and anhydride were heated with phosphorus pentoxide at 180°. The mass darkened considerably; and from it a substance crystallizing like the anil from alcohol and chloroform was obtained. It could not be obtained free from the product of decomposition; its melting-point was about 176°. By long heating with acid, or more quickly by heating to 170° with hydrochloric acid, the anilido acid is converted into orthosulphobenzoic acid.

Paratoluidine Benzparatoluidoorthosulphonate,



$C_6H_4\left<\begin{matrix}CO.NHC_7H_7\\SO_3NH_3C_7H_7\end{matrix}\right.$.—As in the case of aniline apparently only one substance was formed by action of paratoluidine. The mass as obtained was very soluble in hot water, and separated on cooling as a thick oil, which on long standing (six or eight weeks) covered by water, slowly began to crystallize. The crystals first appearing were removed from the oil to another part of the beaker and grew in small clusters as short, sharply-pointed needles.

I. 0.1530 gram gave 0.0111 gram N (Kjeldahl).

II. 0.1402 gram gave 0.0826 gram $BaSO_4$.

	Calculated.	I.	II.
S	7.98	....	8.10
N	6.97	7.25	...

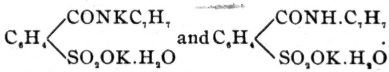
Barium Benztoluidosulphonate crystallized in radiate nodules, sometimes forming a crust on the sides of the beaker and on top of the liquid. Successive crystallization indicated that it was a basic salt, and no formula could be calculated from the analyses:

I. 0.3848 gram lost 0.0260 gram at 150° and gave 0.1199 gram $BaSO_4$.

II. 0.4186 gram lost 0.0280 gram at 150° and gave 0.1312 gram $BaSO_4$.

	I.	II.
Ba	18.34	18.43
H_2O	6.75	6.80

Potassium Salts,



$C_6H_4 \Big\langle \begin{matrix} CONKC_7H_7 \\ SO_2OK.H_2O \end{matrix}$ and $C_6H_4 \Big\langle \begin{matrix} CONH.C_7H_7 \\ SO_2OK.H_2O \end{matrix}$.

These salts crystallized in radiating clusters, and were separated by fractional precipitation of the alcoholic solution by ether. The former salt was obtained pure, the latter not.

I. 0.3233 gram lost 0.0161 gram at 140°.

II. 0.2720 gram lost 0.0134 gram at 140° and gave 0.1238 gram K_2SO_4.

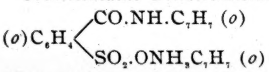
III. 0.2190 gram gave 0.0975 gram K_2SO_4.

	Calculated for $C_{14}H_{11}SO_4K_2.H_2O$.	Found. I.	II.	III.
H_2O	4.70	4.97	4.93	....
K	20.20	....	20.41	19.93

The free *benztoluidosulphonic acid* was obtained, by treating the barium salt with sulphuric acid, as a thick uncrystallizable mass.

Action of Phosphorus Pentachloride.—The potassium salt was treated with phosphorus pentachloride, and the mass treated with water. The resulting substance was crystallized from alcohol and identified as the paratolil described by Remsen and Coates.[1] By heating with acid at 180° the salts are converted into salts of orthosulphobenzoic acid.

Orthotoluidine Benzorthotoluidoorthosulphonate,



$$(o)C_6H_4\left\langle\begin{array}{l}CO.NH.C_7H_7\ (o)\\ SO_2.ONH_3C_7H_7\ (o)\end{array}\right.$$

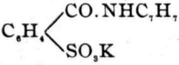
, was formed by the action of the anhydride upon orthotoluidine. The salt crystallized more readily than the analogous para compound, in nodules of radiating needles.

I. 0.2455 gram gave 0.1520 gram $BaSO_4$.
II. 0.2069 gram gave 0.1235 gram $BaSO_4$.
III. 0.2233 gram gave 0.1312 gram $BaSO_4$.
IV. 0.2013 gram gave 0.0112 gram N (Kjeldahl).

	Calculated for $C_{21}H_{22}N_2SO_4$.	Found.			
		I.	II.	III.	IV.
S	7.98	8.50	8.19	8.07	....
N	6.97	....	....	....	6.70

Barium Benztoluidosulphonate crystallized in radiating nodules. It was probably a mixture of a basic salt and the normal. No simple formula could be calculated.

Potassium Benztoluidosulphonate,



$$C_6H_4\left\langle\begin{array}{l}CO.NHC_7H_7\\ SO_3K\end{array}\right.$$

, crystallized in sharply-pointed, brittle, white needles in nodules.

I. 0.2010 gram gave 0.0538 gram K_2SO_4.
II. 0.3227 gram gave 0.0870 gram K_2SO_4.
III. 0.2607 gram gave 0.0725 gram K_2SO_4.

	Calculated.	I.	II.	III.
K	11.88	12.01	12.09	12.49

There was also a potassium salt probably analogous to the one described under the paratoluidine derivatives, but it could not be obtained in pure condition.

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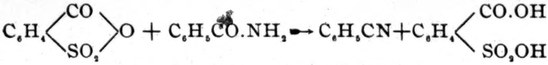
[1] *Loc. cit.*

On heating the salts with acid at 180°, they are converted to salts of orthosulphobenzoic acid.

The potassium salt was treated with phosphorus pentachloride, and on treating the mass with water, a substance was obtained, which on recrystallization from alcohol, melted at 170° (uncorr.) and was identified as the orthotolil described by Remsen and Coates.

Acid Amides.

Benzamide was boiled with the anhydride in benzene solution. Small crystals (prisms) separated, and the odor of nitrile was noticed. The mass after removal of the benzene was boiled with water, and, on cooling, crystals separated which were identified as benzoic acid. The solution was found to contain the acid ammonium salt of orthosulphobenzoic acid. Nothing else could be found. The action is that of dehydration:



$$C_6H_4\left\langle\begin{matrix}CO\\SO_2\end{matrix}\right\rangle O + C_6H_5CO.NH_2 \rightarrow C_6H_5CN + C_6H_4\left\langle\begin{matrix}CO.OH\\SO_2OH\end{matrix}\right.$$

$$C_6H_5CN + 2H_2O \rightarrow C_6H_5COOH + NH_3.$$

Acetamide acted like benzamide but with more difficulty,

$$CH_3CONH_2 - H_2O \rightarrow CH_3CN.$$

Phosphorus pentachloride acting on the anhydride produced both chlorides of orthosulphobenzoic acid. The action was exceedingly variable, depending upon the purity of the chemicals, the temperature and time of action. With pure dry chemicals it was impossible to secure action below 120°. A small amount of oxychloride considerably lowered the temperature. At 20° no action took place even though the mass was moistened with phosphorus oxychloride.

It was concluded from numerous experiments that the formation of the *unsymmetrical chloride* was favored by high temperature, continued action and excess of pentachloride. The same results were noted in the action of the pentachloride on the potassium salts.

Conclusion.

In the foregoing it has been shown that the anhydride of orthosulphobenzoic acid is a well-characterized stable substance.

Many of the sulphonphthaleïns are readily obtained in pure condition, and they are possessed of marked color, analogous to the phthaleins, which they resemble.

A series of sulphonic acids has been formed isomeric with the sulphaminebenzoic acids from which they are distinguished by their solubility, and into which they can be converted by the successive action of phosphorus pentachloride and alkaline hydroxide.

Contributions from the Chemical Laboratories of the Massachusetts Institute of Technology.

XIX.—IODOMETRIC ESTIMATION OF TELLURIUM.

By James F. Norris and Henry Fay.

Tellurium is estimated accurately with difficulty. Of the two gravimetric methods, weighing as the dioxide and in the elementary state, the former alone is accurate. When determined as the dioxide, tellurium is separated from other elements and oxidized with dilute nitric acid. After evaporation of the solution to dryness the basic nitrate is transferred to a crucible and heated to fusion. On account of the time required the determination is shortened by weighing the precipitated tellurium after drying at 110°. Brauner[1] has shown, however, that the results obtained in this way are not reliable. The finely divided tellurium is slowly oxidized in the strong hydrochloric acid solution required for the precipitation with sulphur dioxide, forming tellurium tetrachloride which remains in solution. When tellurium is washed and dried it slowly oxidizes and the weight found is, consequently, too great. It was shown that precipitated tellurium increased in weight about 0.5 per cent. during washing and drying for two hours at 110°. As these two sources of error tend to neutralize each other, the result obtained is approximately correct.

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[1] J. Chem. Soc., **55**, 392.

Brauner[1] has made a careful study of a number of reactions of tellurium with the view of using them for its volumetric estimation. He found that the reactions between tellurium dioxide and stannous chloride, potassium bichromate, iodine, or potassium permanganate in acid solution, could not be made the basis of an accurate method, but that the oxidation of tellurium dioxide with potassium permanganate in alkaline solution proceeded regularly. The excess of permanganate was determined, after acidifying with sulphuric acid, by adding an excess of oxalic acid and titrating back with permanganate. When the solution was acidified part of the permanganate was decomposed and oxygen and ozone were liberated. The amount of decomposition depends upon the quantity of sulphuric acid used and upon the concentration of the solution. Brauner found that by working under definite conditions there was a constant source of error which amounted to 0.35 per cent., and by deducting this amount satisfactory results could be obtained. This method cannot be used in the presence of the halogen acids.

Gooch and Morgan[2] have recently proposed a method for the estimation of tellurium based on the insolubility of the iodide in strong sulphuric acid. To the solution of tellurium dioxide is added sulphuric acid in such quantity, that after mixing with the potassium iodide solution the concentration of the acid is not less than 25 per cent. by volume. A standard solution of potassium iodide is added until no further precipitation takes place. The results are fairly accurate when less than 0.1 gram of tellurium dioxide is used for analysis.

As work requiring the rapid estimation of tellurium in presence of the halogen acids is in progress in this laboratory, a new method was sought. The method recently proposed by us[3] for selenium was applied to tellurium. It was shown that one molecule of selenous acid reacts with four of sodium thiosulphate in the presence of dilute acids. A similar reaction takes place with tellurous acid but the end-point is not sharp, because the addition of sodium thiosulphate produces a yellow solution, and the reduced tellurium compound is slowly oxidized by iodine. By observing the first appearance of a greenish color, however, the amount of tellurium dioxide could be approximately determined.

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[1] J. Chem. Soc., **59**, 58, 238.

[2] Ztschr. anorg. Chem., **13**, 169.

[3] This JOURNAL, **18**, 703

As the results were not positive, another method was studied, namely, oxidation of tellurous to telluric acid by potassium permanganate and estimation of the excess of the latter by treating with potassium iodide and sulphuric acid, and titrating the liberated iodine with sodium thiosulphate. Brauner has shown that the oxidation of tellurous acid to telluric acid in alkaline solution takes place according to the following equation :

$$(1) \quad 2KMnO_4 + 3TeO_2 = K_2O + 2MnO_2 + 3TeO_3.$$

The manganese dioxide is not precipitated, but remains in solution, probably as a manganite or in combination with telluric acid, forming a compound analogous to the salt $MnO_2.SO_3$. If to such a solution potassium iodide and sulphuric acid be added, the following reaction takes place :

$$(2) \quad 2MnO_2+4KI+4H_2SO_4 = 2MnSO_4+2K_2SO_4+4H_2O+4I.$$

Any excess of permanganate will react as follows :

$$(3) \quad 2KMnO_4 + 10KI + 8H_2SO_4 = 2MnSO_4 + 6K_2SO_4 + 8H_2O + 10I.$$

Combining equations (1) and (2) the oxidation of tellurium dioxide may be expressed in this way :

$$(4) \quad 2KMnO_4 + 3TeO_2 + 4KI + 5H_2SO_4 = 3TeO_3 + 3K_2SO_4 + 2MnSO_4 + 5H_2O + 4I.$$

It is seen from equation (4) that 2 molecules of potassium permanganate in the presence of tellurium dioxide will liberate 4 atoms of iodine, whereas from equation (3) the same amount of permanganate will liberate 10 atoms of iodine. There is, therefore, a deficit of 6 atoms of iodine for 3 molecules of tellurium dioxide, or 1 molecule of the latter produces a deficit of 2 atoms of iodine, or 2 molecules of sodium thiosulphate. This deficit is obtained by subtracting from the amount of thiosulphate equivalent to the permanganate, equation (3), the amount required to react with the iodine liberated in the presence of tellurium dioxide. This method gives accurate results, can be used in the presence of halogen acids, and does not require a factor-correction for the decomposition of the potassium permanganate.

Certain precautions are necessary in order that accurate results may be obtained ; the oxidation must take place in the presence of a large excess of alkali, and the solution must be dilute and cold in order to prevent the reduction of the telluric acid by the hydriodic acid.

The tellurium dioxide used to test the method was prepared in the following manner : A sample of tellurium containing traces of copper and selenium was precipitated with sulphurous acid, oxidized with nitric acid, evaporated to dryness, and fused. The oxide so obtained was dissolved in hot sodium hydroxide and precipitated with grape-sugar. The tellurium was again oxidized, and from the oxide the basic nitrate was obtained by crystallization from nitric acid (sp. gr. 1.25). After two crystallizations the basic nitrate, which was obtained in well-developed crystals 5–6 mm. in length, was decomposed into the oxide just below red heat. The resulting white powder was fused quickly in small portions. In this way pure, perfectly white, tellurium dioxide was obtained. Staudenmaier[1] states that it is difficult to get tellurium dioxide without a brown color, due to a minute trace of free tellurium. Fusion of the nitrate directly always causes the separation of traces of tellurium, but by proceeding as directed above, decomposing below a red heat, and then fusing, the oxide can be obtained in pure condition. A standard solution of the oxide was made by dissolving about 2.5 grams in a small amount of sodium hydroxide and diluting to 500 cc.

An approximately one-tenth normal solution of sodium thiosulphate was standardized against iodine, which had been dried over sulphuric acid and sublimed from one-third of its weight of potassium iodide. 1 cc. $Na_2S_2O_3 = 11.21$ mg. I.

A solution of potassium permanganate was made by dissolving about 7 grams of the salt in 1 liter of water. This was titrated against sodium thiosulphate in the following manner : To 20 cc. of the potassium permanganate, diluted to 400 cc. with ice-water, were added 10 cc. of a solution of potassium iodide, containing 2 grams of the salt, and dilute sulphuric acid until the solution became clear. The iodine liberated was equivalent to 49.90 cc. of sodium thiosulphate. In order to determine whether the reaction between potassium permanganate and potassium iodide in acid solution takes place as represented by equation (3), the permanganate was standardized against acid potassium oxalate. The same value was obtained by both methods.

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[1] Ztschr. anorg. Chem., **10**, 206.

In estimating tellurium a portion of the standard solution of the oxide was measured off and about 20 cc. of a 10 per cent. solution of sodium hydroxide added. Potassium permanganate was added until the meniscus of the brown solution showed a deep pink color. The solution was diluted with ice-water, treated with potassium iodide and sulphuric acid, and titrated as above.

The results obtained by this method, together with the amount of solutions used, are given in the following table. The quantity of sodium thiosulphate in each case is the amount equivalent to the iodine set free in the presence of tellurium dioxide. By subtracting these values from the amount equivalent to the potassium permanganate used, the deficit is obtained. 1TeO_2 causes a deficit of 2$Na_2S_2O_3$:

TeO_2 taken. Gram.	$KMnO_4$. cc.	$Na_2S_2O_3$. cc.	TeO_2 found. Gram.	Te. Per cent.
0.1507	20	28.58	0.1504	79.80
0.1507	20	28.55	0.1506	79.91
0.1758	25	37.39	0.1762	80.15
0.1758	25	37.48	0.1756	79.86
0.2009	30	46.38	0.2008	79.93
0.2009	30	46.40	0.2007	79.88
0.1562	20	27.79	0.1560	79.84
0.1824	25	36.50	0.1825	80.00
			Theory,	79.94

The first six results were obtained by using portions of the standard solution of tellurium dioxide; the last two by using portions weighed directly. The table contains a series of eight consecutive determinations. In calculating the results, 127.6 has been taken for the atomic weight of tellurium.

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In order to test the accuracy of the method in the presence of the halogen acids, the double bromide of tellurium and potassium was analyzed. The salt was prepared by dissolving the theoretical quantities of tellurium dioxide and potassium bromide in hydrobromic acid and evaporating to crystallization. After recrystallization from a hot saturated solution the salt was dried at 120° for three hours. The following is a series of consecutive results :

K_2TeBr_6 taken. Gram.	$KMnO_4$. cc.	$Na_2S_2O_3$. cc.	Te. Per cent.
0.8823	30	45.62	18.59
0.7134	25	38.79	18.64
0.5472	20	31.88	18.58
0.5679	20	31.11	18.66

Theory, 18.61

A series of experiments showed that this method of analysis could also be applied to the determination of selenium, but it offers no advantages over the simpler method already proposed by us.

BOSTON, MASS., January, 1898.

Contribution from the Chemical Laboratory, University of Oregon.

THE RELATION OF TRIVALENT TO PENTAVALENT NITROGEN.

BY ARTHUR LACHMAN.

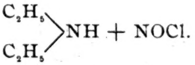
The following lines contain a preliminary account of a few experiments undertaken for the purpose of investigating the subject of this brief paper. The experiments are fragmentary, but for the present I cannot continue them. In publishing this note, I wish to secure for myself the right to take up the work again as soon as I can find the opportunity to do so.

The idea is by no means new that the peculiarities of nitrogen compounds may find their explanation in the variability of the valence of their nitrogen atoms. Innumerable well-known facts illustrate the tendency of nitrogen to pass from one state of valence to the other. Indeed, most attempts to explain the reactions of nitrogen compounds are based upon the assumption of some such relation. While many of these speculations rest upon a tolerably safe foundation, many others are very vague; nearly all have one feature in common; *viz.*, arbitrariness. The following experiments were undertaken for the purpose of determining the actual limits within which such speculations must remain.

For certain theoretical reasons, which need not be discussed as yet, the secondary nitrosamines were first taken up. These substances contain, in all likelihood, two trivalent nitrogen atoms of diverse chemical character, $R_2 = \overset{III}{N} - \overset{III}{N} = O$, and, therefore, seemed to afford a good starting-point for the study of addition reactions. So far, their behavior towards hydrochloric acid, zinc ethyl, and hydroxylamine has been investigated.

Nitrosamines with Hydrochloric Acid.

Both dimethyl- and diethylnitrosamine form hydrochlorides.[1] These salts are very unstable, and at a slightly elevated temperature break down. On heating them in a sealed tube to about 60°, the tube becomes filled with deep-red fumes, and upon cooling down, crystals of dimethyl- (or diethyl-) amine hydrochloride appear. If a rapid stream of hydrochloric acid gas is passed into diethylnitrosamine, the liquid becomes hot, nitrosyl chloride passes off, and diethylamine hydrochloride remains behind, the nitrosamine being completely decomposed:



$$\begin{matrix} C_2H_5 \\ C_2H_5 \end{matrix}\Big\rangle NH + NOCl.$$

More interesting results were obtained with diphenylnitrosamine. A solution of this substance in benzene (carefully dried over sodium) was treated with a mixture of hydrochloric acid gas and carbon dioxide (both dried over phosphorus pentoxide). The carbon dioxide served to exclude the air and to moderate the action. The vessel containing the nitrosamine was kept cooled with water, and the gases emerging from it conducted into a solution of potassium iodide. The gas finally escaping turned brown in the air, showing that it contained nitric oxide. The iodine set free was titrated with sodium thiosulphate:

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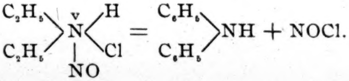
[1] Dimethylnitrosamine hydrochloride has been described by Renouf (Ber. d. chem. Ges., **13**, 2170). The salt of diethylnitrosamine is an oil which solidifies below 0°.

1.00 gram nitrosamine required 24.5 cc. 1/5 N thiosulphate.

	Gram.
Iodine calculated	0.641
" found	0.622

It will thus be seen that very nearly the calculated amount of iodine was set free, showing that at the ordinary temperature diphenylnitrosamine takes up *dry* hydrochloric acid, and immediately splits off nitrosyl chloride:



$$\left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right>\underset{\underset{NO}{|}}{\overset{\text{v}}{N}}\left<\begin{matrix}H\\Cl\end{matrix}\right. = \left.\begin{matrix}C_6H_5\\C_6H_5\end{matrix}\right>NH + NOCl.$$

The residue in the flask formed a black tar, and no attempt was made to find diphenylamine in it.

The combination, $R_2{=}N\left<\begin{matrix}H\\Cl\\NO\end{matrix}\right.$, then, is a very unstable one, and readily breaks down into simpler molecules containing trivalent nitrogen. This is in exact analogy with the addition-products of the isonitriles discovered by Nef, in which the bivalent carbon atom readily takes up various substances, and as readily splits them off.

Nitrosamines with Zinc Ethyl.

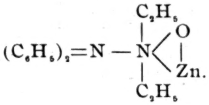
Diethylnitrosamine does not react with zinc ethyl in the cold, even after standing several weeks. On warming to 100°, reaction takes place rapidly, accompanied by almost complete decomposition. Basic gases are given off, and a tarry substance remains which has basic properties, reduces silver nitrate, and does not yield crystalline derivatives.

Diphenylnitrosamine reacts violently with zinc ethyl in the cold. If the reaction is carried out in dilute benzene solution, with molecular quantities of the substances, the solvent soon becomes warm, and frequently boils. The solution is kept boiling for about an hour, and then carefully evaporated in a stream of dry carbon dioxide. A gelatinous mass remains, which crumbles to a yellow powder when rubbed on a porous plate. The powder is amorphous; it melts at about 135°, is insoluble in all ordinary solvents, and apparently is quite stable in air. It is an addition-product formed from one molecule each of the reacting substances:

0.2414 gram gave 0.626 gram zinc oxide upon ignition.

	Calculated for $(C_6H_5)_2N.NO.Zn(C_2H_5)_2$.	Found.
Zinc	20.8	20.3

Its constitution is at present unknown. On treatment with water or alcohol, the substance is decomposed *without* evolution of gas; the products are zinc hydroxide, diphenylamine (melting-point 53.5°; diphenylamine reaction) and an unstable base. This base is slightly volatile with water vapor, and reduces Fehling's solution in the cold; its hydrochloric acid solution gives off ethyl chloride on boiling. Possibly the structure is to be represented as follows, which would account for the formation of diphenylamine and a reducing base (diethylhydroxylamine?), as well as for the absence of gases upon decomposition with water:



Here again we notice how readily a pentavalent nitrogen atom passes into the trivalent state. A number of other substances have been subjected to the action of zinc ethyl, but no report can be made as yet.

Nitrosamines with Hydroxylamine.

As a general rule, nitrosamines fail to show any condensation-reactions; their behavior with hydroxylamine seems to form an exception. The reaction of this substance with diethylnitrosamine is so curious, however, that I should prefer to wait for more evidence before presenting the facts.

Diphenylnitrosamine and hydroxylamine react quite readily. Though no new body could be isolated as the product, it was possible to follow the reaction quantitatively. If molecular quantities of the two substances are boiled in methyl-alcoholic solution, either in the presence or absence of free alkali, nitrous oxide is given off in theoretical quantity, and there remains only diphenylamine (19 grams from 25 grams nitrosamine ; calculated, 21 grams) :

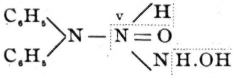
1.0 gram nitrosamine gave 113 cc. moist nitrous oxide at 10° and 737 mm.

	Gram.
Nitrous oxide calculated	0.22
" " found	0.20

At no time during the reaction, which lasts from fifteen minutes to an hour (the more alkali present the shorter the duration), can any trace of hyponitrites be discovered, even in the presence of a very large excess (two molecules) of alkali. The appearance of nitrous oxide can therefore not be accounted for by the intermediate formation and decomposition of hyponitrous acid :[1]

$$(C_6H_5)_2=N-N=O+H_2NOH=(C_6H_5)_2NH+HON=NOH,$$

but only by the direct decomposition of the addition-product as indicated in the following formula :



Again we have the curious splitting down of a pentavalent derivative of diphenylnitrosamine into the trivalent diphenylamine, at the low temperature of boiling methyl alcohol.

It is thus seen that very decided limits exist for the stability of pentavalent nitrogen compounds. By a proper choice of radicals, they may be made to break down spontaneously or upon very slight provocation. By continuing along the lines laid down, it will perhaps be possible to ascertain the nature and the amount of contrast among its attached groups of atoms which suffices to make the pentavalence of nitrogen unstable. On the other hand, we must not forget that a certain amount of diversity among the groups is necessary for the existence of the pentavalent state. No pentavalent nitrogen compound is known in which all five radicals are alike in chemical character. An attempt to prepare such a compound, about two years ago,[1] proved abortive; renewed efforts in the same direction have borne no results. The pentavalence of nitrogen, then, is determined by the contrast of the attached groups of atoms, it being possible to have too little as well as too much of this *sine qua non*. The work will be taken up again as soon as possible. This brief note is *not* intended to "reserve the field," but on the contrary to urge others to help in its cultivation.

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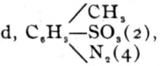
[1] Since hyponitrites are stable in the presence of alkali.

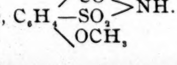
EUGENE, OREGON, Jan., 1898.

ON PARAMETHOXYORTHOSULPHOBENZOIC ACID AND SOME OF ITS DERIVATIVES.

BY P. R. MOALE.[2]

Preparation.

The preparation of the above acid involves several stages, the starting-point being paratoluidineorthosulphonic acid. The directions of Parks[3] were followed in the main; when differences occur, mention of them is made. Parks found that only the methoxy product was formed when paradiazoorthotoluenesulphonic acid,  $C_6H_3\left\langle\begin{array}{l}CH_3\\SO_3(2)\\N_2(4)\end{array}\right.$, is boiled with absolute methyl alcohol under ordinary, diminished, or increased pressure. So the diazo compound prepared according to the directions of Parks was at once converted into the paramethoxyorthotoluenesulphonic acid at ordinary pressure, and the acid was converted into the sulphonamide through the chloride.

The sulphonamide was then oxidized with potassium permanganate to the sulphinide,  $C_6H_3\left\langle\begin{array}{l}\left.\begin{array}{l}CO\\SO_2\end{array}\right>NH\\OCH_3\end{array}\right.$.

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[1] Lachman: This JOURNAL, **18**, 372.

[2] This article and the following one are from the dissertation submitted by the author to the Board of University Studies of the Johns Hopkins University, for the degree of Doctor of Philosophy, June, 1894.

[3] This JOURNAL, **15**, 320.

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The best conditions were found to be as follows: To use the same amount of sulphonamide and potassium permanganate as given by Parks, and to increase the quantity of water to 2 liters, and to this solution to add from 3 to 5 grams of potassium hydrate.

The time required for the oxidation was about the same, from three to four hours. This treatment increased the yield of the sulphinide to between 25 and 30 per cent. From the filtrate of the sulphinide Parks first obtained potassium chloride, and then the acid potassium salt of paramethoxyorthosulphobenzoic acid, crystallized out, while it was found here that by careful evaporation the acid potassium salt first crystallized out. The salt was identified by analysis.

I. 0.1548 gram of salt lost 0.0098 gram of H_2O.

II. 0.2362 gram of dehydrated salt gave 0.0750 gram of K_2SO_4.

	Calculated for	Found.	
	$C_6H_3\begin{array}{l}/OCH_3 \\ -SO_3K.H_2O. \\ \backslash COOH\end{array}$	I.	II.
H_2O	6.25	6.33	....
K (dehydrated)	14.44	....	14.38

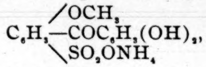
The acid potassium salt can also be made by oxidizing with potassium permanganate the potassium salt of paramethoxyorthotoluenesulphonic acid. This was tried as directed by Parks, but as the yield was not as good as through the paramethoxysulphinide, the latter method was adopted. The salt was identified by analysis.

0.2689 gram of salt lost 0.0169 gram of H_2O and gave 0.0810 gram of K_2SO_4.

	Calculated for $C_6H_3\begin{array}{l}/OCH \\ -SO_3K.H_2O. \\ \backslash COOH\end{array}$	Found.
H_2O	6.25	6.28
K	13.58	13.52

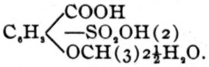
Parks's directions for the conversion of the paramethoxysulphinide and the acid potassium salt of paramethoxyorthosulphobenzoic acid into the free paramethoxyorthosulphobenzoic acid, were followed. The conversion of the acid potassium salt was found to take place as stated by Parks, but the transformation of the paramethoxysulphinide into the acid was found to take place somewhat differently, as will be shown further on.

Conversion of Paramethoxybenzoic Sulphinide into Paramethoxyorthosulphobenzoic Acid.

The sulphinide was placed in a balloon-flask; to it was added a sufficient quantity of water and hydrochloric acid, 8 parts of water to 1 part of concentrated hydrochloric acid by weight. The balloon-flask was connected with an inverted condenser, and the liquid boiled until all the paramethoxybenzoic sulphinide was dissolved. The contents of the flask were then evaporated to crystallization. On cooling, long, white needles crystallized out. These were recrystallized. Thinking this was the acid ammonium salt of paramethoxyorthosulphobenzoic acid, the attempt was made to convert it into the ammonium salt of paramethoxydioxybenzoylbenzenesulphonic acid,  $C_6H_3\begin{matrix} / OCH_3 \\ -COC_6H_3(OH)_2 \\ \backslash SO_2ONH_4 \end{matrix}$, by treatment with resorcin, but a sulphonfluoresceïn was obtained. This indicated that the substance used must have been the free paramethoxyorthosulphobenzoic acid. The same experiment was made with the same and different specimens, with like results in all cases. The melting-point was taken and the crystals melted at 104°, the melting-point of paramethoxyorthosulphobenzoic acid, thus showing that the free acid instead of the acid ammonium salt, is formed by boiling paramethoxybenzoic sulphinide with water and hydrochloric acid, as directed above. Again, the substance was treated with sodium hydrate, and no odor of ammonia could be detected, nor its presence shown by litmus paper. Other properties of the acid were tested and they agreed with Parks's description of paramethoxyorthosulphobenzoic acid. It melted without decomposition at 104°, and, on cooling, it quickly solidified, and again melted at the same point. From the solution ammonium chloride was obtained and isolated as a product of the reaction; it was separated from the free acid by crystallization from water and alcohol.

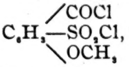
This formation of the acid directly from the sulphinide by boiling with water and hydrochloric acid is not in accordance with that described by Remsen and Linn[1] and others, who in the case of the simple benzoic sulphinide obtained the acid ammonium salt of orthosulphobenzoic acid by the above-mentioned method. The above experiments were performed repeatedly, different specimens of paramethoxysulphinide being used, and in every case the paramethoxyorthosulphobenzoic acid, melting at 104°, was obtained.

Paramethoxyorthosulphobenzoic Acid,



$C_6H_3\left\langle\begin{array}{l}COOH\\ —SO_2OH(2)\\ OCH(3)2\tfrac{1}{2}H_2O.\end{array}\right.$

This acid was prepared according to the method just described, from paramethoxybenzoic sulphinide, by boiling with 8 parts of water to 1 part of concentrated hydrochloric acid by weight. It was also prepared from its acid potassium salt, which is formed along with the paramethoxybenzoic sulphinide when paramethoxyorthotoluenesulphonamide is oxidized with potassium permanganate. The acid potassium salt is converted into the acid chloride, $C_6H_3\begin{array}{l}/COCl\\ —SO_2Cl\\ \backslash OCH_3\end{array}$, by phosphorus pentachloride, and this by boiling with water into paramethoxyorthosulphobenzoic acid. It is very soluble in water, from which it crystallizes in long, transparent, colorless needles. It melts at 104°, and, on cooling, quickly solidifies, and melts again at the same point on heating. This may be repeated without change in the melting-point.



Analyses gave the following results :

I. 0.1698 gram of substance gave 0.0619 gram of H_2O, and 0.2165 gram of CO_2.

II. 0.1758 gram of substance gave 0.0675 gram of H_2O, and 0.2238 gram of CO_2.

III. 0.1691 gram of substance gave 0.1494 gram of $BaSO_4$ (Liebig method).

IV. 0.1633 gram of substance gave 0.1408 gram of $BaSO_4$ (Liebig method).

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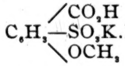
[1] This JOURNAL, II, 73.

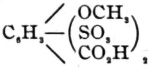
	Calculated for $C_6H_3\begin{matrix}/CO_2H\\ -SO_3H(2)2\frac{1}{2}H_2O.\\ \backslash OCH_3(4)\end{matrix}$	Found. I.	II.	III.	IV.
C	34.77	34.77	34.71	....	....
H	4.69	4.05	4.27	....	....
S	11.72	....	....	12.14	11.84

The method of combustion used in these analyses and in those of the sulphonfluoresceïns is that of de Roode.[1]

Acid Potassium Salt,  $C_6H_3\begin{matrix}/CO_2H\\ -SO_3K.H_2O.\\ \backslash OCH_3\end{matrix}$—This salt was obtained in the course of preparation of the paramethoxyorthosulphobenzoic acid in several ways as already described. It is very soluble in water, less so in alcohol. Analyses gave the following results:

0.2689 gram of salt lost 0.0169 gram of H_2O and gave 0.081 gram K_2SO_4.

	Calculated for $C_6H_3\begin{matrix}/CO_2H\\ -SO_3K.H_2O.\\ \backslash OCH_3\end{matrix}$	Found.
H_2O	6.25	6.28
K	13.58	13.52

Acid Calcium Salt,  $C_6H_3\left(\begin{matrix}OCH_3\\ SO_3\\ CO_2H\end{matrix}\right)_2Ca.4H_2O.$ — This was prepared from the free acid. It is extremely soluble in water. Very slow evaporation is necessary to produce good crystals, and the specimen of the salt analyzed stood over a month before crystals separated that were suitable for analysis.

Analyses gave the following results:

I. 0.0458 gram of salt lost at 135° 0.0058 gram H_2O.

II. 0.0282 gram of salt lost at 135° 0.0035 gram of H_2O.

III. 0.0658 gram of salt gave 0.0138 gram of $CaSO_4$.

	Calculated for $C_6H_3\left(\begin{matrix}OCH_3\\ SO_3\\ CO_2H\end{matrix}\right)_2Ca.4H_2O.$	Found. I.	II.	III.
H_2O	12.54	12.66	12.41	....
Ca	6.15	....	....	6.17

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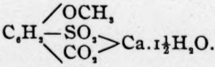
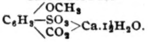
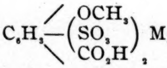
[1] This JOURNAL, **12**, 236.

Neutral Calcium Salt,  $C_6H_3\begin{matrix}/OCH_3\\-SO_3\\\backslash CO_2\end{matrix}{>}Ca.1\tfrac{1}{2}H_2O$.—This is extremely soluble in water and could not be obtained in good crystals. After filtering and evaporating almost to dryness, fine crystal plates separated out. Analysis gave the following results:

0.042 gram of salt lost 0.0037 gram of H_2O and gave 0.0189 gram of $CaSO_4$.

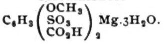
	Calculated for  $C_6H_3\begin{matrix}/OCH_3\\-SO_3\\\backslash CO_2\end{matrix}{>}Ca.1\tfrac{1}{2}H_2O$.	Found.
H_2O	9.09	8.81
Ca	13.46	13.28

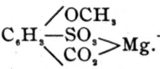
Acid Magnesium Salt,  $C_6H_3\begin{matrix}/\\-\\\backslash\end{matrix}\left(\begin{matrix}OCH_3\\SO_3\\CO_2H\end{matrix}\right)_2Mg.3H_2O$.—This is very soluble in water, but after careful evaporation fine white needles were obtained, which proved to be quite efflorescent.

Analyses gave the following results :

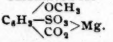
I. 0.0896 gram of the salt lost 0.091 gram of H_2O and gave 0.0176 gram of $MgSO_4$.

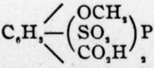
II. 0.056 gram of salt gave 0.0125 gram of $HgSO_4$.

	Calculated for  $C_6H_3\left(\begin{matrix}OCH_3\\SO_3\\CO_2H\end{matrix}\right)_2Mg.3H_2O$.	Found. I.	 II.
H_2O	10.00	10.15	....
Mg	4.44	3.93	4.46

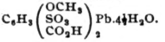
Neutral Magnesium Salt,  $C_6H_3\begin{matrix}/OCH_3\\-SO_3\\\backslash CO_2\end{matrix}{>}Mg$.—It was found impossible to obtain crystals of this salt, as it is extremely soluble. The solution was evaporated to dryness. Analysis of the residue gave the following results :

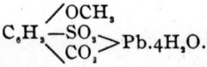
0.0151 gram of salt gave 0.0073 gram $MgSO_4$.

	Calculated for  $C_6H_3\begin{matrix}/OCH_3\\-SO_3\\\backslash CO_2\end{matrix}{>}Mg$.	Found.
Mg	9.45	9.66

Acid Lead Salt,  $C_6H_3-\left(\begin{matrix}OCH_3\\SO_3\\CO_2H\end{matrix}\right)_2Pb.4\frac{1}{2}H_2O$.—The salt crystallized from concentrated solution in fine white needles. It is very soluble in water, and insoluble in alcohol. Analysis gave the following results:

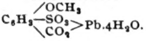
0.0708 gram of salt at 100° lost 0.0075 gram of H_2O and gave 0.0288 gram of $PbSO_4$.

	Calculated for  $C_6H_3\left(\begin{matrix}OCH_3\\SO_3\\CO_2H\end{matrix}\right)_2Pb.4\frac{1}{2}H_2O$.	Found.
H_2O	10.8	10.59
Pb	27.60	27.79

Neutral Lead Salt,  $C_6H_3\begin{matrix}/OCH_3\\-SO_3\\\backslash CO_2\end{matrix}>Pb.4H_2O$.—Short, fine, white needles, very soluble in water. Analysis gave the following results:

I. 0.0667 gram of salt gave 0.0395 gram of $PbSO_4$.

II. 0.0516 gram of salt lost 0.0073 gram of H_2O at 115°, and gave 0.0304 gram of $PbSO_4$.

	Calculated for  $C_6H_3\begin{matrix}/OCH_3\\-SO_3\\\backslash CO_2\end{matrix}>Pb.4H_2O$.	Found. I.	Found. II.
H_2O	14.14	....	14.15
Pb	40.66	40.46	40.25

Attempt to Obtain an Anhydride.

About 2 to 3 grams of paramethoxyorthosulphobenzoic acid were placed in a test-tube and gradually heated gently over a free flame and in a sulphuric-acid bath. At 100° it lost its water of crystallization, and at 104° melted. On heating to 145° it again lost water, which condensed on the walls of the tube, and crystals sublimed in the upper part of the vessel. They were fine needles. It was found impossible to get possession of them in sufficient quantity for analysis. Upon higher heating the compound broke down, yielding products which had a most disagreeable, nauseating odor.

Paramethoxysulphonfluoresceïn.

The first experiment was to introduce 2 molecules of resorcinol into the paramethoxyorthosulphobenzoic acid. Both the resorcinol and the acid were carefully dehydrated and then heated together in the proportion of 1 molecule of acid to 2 molecules of resorcinol. The method of procedure was as follows: The correctly calculated amounts of the dehydrated acid and resorcinol were placed together in a small beaker, which was placed in a sulphuric-acid bath. Suspended from above was a thermometer reaching into the mixture; this could also be used as a stirring rod. Heat was applied very gently and slowly to the bath. At 65° the resorcinol began to melt, and gradually melted until 75° was reached, the mixture becoming wine-red in color. A few crystals of resorcinol sublimed into the upper part of the beaker. The heat was gradually raised until 110°–115° was reached, and the thermometer kept at that temperature as long as the reaction would permit. The reaction went smoothly at that temperature. Stirring must be kept up all the time, as it is necessary for the reaction, otherwise it appears not to take place. When the mixture is stirred, the temperature rises and the source of heat is removed. This same rise of temperature and the necessity of stirring were noted by Blackshear.[1]

After heating for two hours the mass became viscid and reddish-black. It became solid on slight lowering of the temperature, and in some cases it was necessary to raise the temperature in order to keep the mass liquid. On cooling, the fused mass solidified and the surface was glossy with a resinous luster. The cooled mass was then treated with water to dissolve out any unchanged resorcinol or acid and other soluble matter. The fused mass was then dissolved in sodium hydrate, and precipitated with hydrochloric acid, when the sulphonfluoresceïn comes down as a reddish, granular mass. This was washed thoroughly with hot and cold water by decantation. It was then brought on a filter, and by the aid of a filter-pump washed again. The washing of the sulphonfluoresceïn is very important. In drying the substance great difficulties were encountered. When dried on a drying-plate it lost water, as was shown by analysis. Next, drying over sulphuric acid was tried, and in this case also it lost water. The best method was found to be to dry it as thoroughly as possible by the aid of the filter-pump, allow it to stand over night, and then dry it between sheets of drying paper. It then appeared as a brown-red, amorphous mass. This was finely ground for analysis.

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[1] This JOURNAL, **14**, 455.

The substance was very difficult to burn, and the analytical results indicate that an impure sulphonfluoresceïn was formed. Different specimens were analyzed several times, but no constant results could be obtained. Analyses gave the following figures:

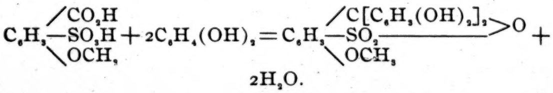
0.0802 gram of the substance gave 0.1688 gram of CO_2, and 0.0384 gram of H_2O.

	Calculated for $C_{20}H_{16}O_8S$.	Found.
C	57.69	57.15
H	3.87	5.31

Another analysis gave C 59.30 per cent. and H 5.49 per cent.

An analysis for sulphur gave S 6.44 per cent., while the calculated percentage for the above formula is S 7.39 per cent.

The sulphonfluoresceïn is insoluble in all ordinary solvents; soluble in caustic alkali with a beautiful red-green fluorescence. It is precipitated by hydrochloric acid from its alkaline solution as a red-brown granular mass. In the main the reaction no doubt takes place as represented in this equation:



$$C_6H_3\left\{\begin{matrix}CO_2H\\SO_3H\\OCH_3\end{matrix}\right. + 2C_6H_4(OH)_2 = C_6H_3\left\{\begin{matrix}\left.\begin{matrix}C[C_6H_3(OH)_2]_2\\SO_2\end{matrix}\right\rangle O\\OCH_3\end{matrix}\right. + 2H_2O.$$

Preparation of the Orcinol Compound.

Orcinol was substituted for resorcinol in the hope of getting a purer product. The method of procedure was the same as in the case of the resorcinol. The orcinol melted at 65°-75°, and reaction began at 110°, water being given off. The temperature in this case had to be raised to 145° in order to complete the reaction, stirring being kept up all the time. The manner of washing, filtering, dissolving, precipitating, and drying was the same as in the case of the resorcinol compound. The yield was about 50 per cent. The orcinol product is a better substance to deal with than the sulphonfluoresceïn obtained with resorcinol. The same difficulties in drying were also encountered here. In alkaline solution it gives a similar fluorescence, and is precipitated by hydrochloric acid from its alkaline solution.

An analysis was made to determine whether there was water in the compound. The substance was heated at 110°–115° with loss of water, and on raising the temperature no more water was given off.

The analysis gave the following results:

I. 0.0578 gram of substance at 110°–115° lost 0.0024 gram of H_2O.

II. 0.0529 gram of substance gave 0.0271 gram of H_2O, and 0.1140 gram ot CO_2.

III. 0.0602 gram of substance gave 0.0312 gram of H_2O, and 0.1314 gram of CO_2.

IV. 0.1076 gram of substance gave 0.0512 gram of $BaSO_4$ (Liebig method).

V. 0.1330 gram of substance gave 0.0634 gram of $BaSO_4$ (Liebig method).

	Calculated for $C_{22}H_{20}O_8S+H_2O$.	Found.				
		I.	II.	III.	IV.	V.
H_2O	3.89	4.15	....	....	....	....
C	57.14	....	58.76	59.07	....	....
H	4.76	....	5.69	5.75	....	....
S	6.92	....	....	....	6.63	6.54

These analyses show that a sulphonfluoresceïn of the above formula was probably formed, but that it was not pure. It was found impossible to purify it. Blackshear also found it impossible to purify the sulphonfluoresceïn formed from orthosulphonbenzoic acid and resorcinol according to the above method. He prepared it from dioxybenzoylbenzenesulphonic acid.[1]

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[1] Sulphonfluoresceïn has since been prepared in pure condition by treating the chlorides of orthosulphobenzoic acid with resorcinol (Remsen and McKee, this JOURNAL, **18**, 802) and by treating the anhydride of the acid with resorcinol (see article by M. D. Sohon in this number).—I. R.

Action of Phenol.—An attempt to introduce two residues of phenol into paramethoxyorthosulphobenzoic acid was tried. The method of procedure was the same as that followed in the case of resorcinol and orcinol. The phenol began to melt at 45° and was all melted at 65°. Slight action began at 85°, and at 105°, on stirring, the thermometer rapidly rose to 130°, indicating reaction, the liquid becoming wine-red in color. The temperature was kept at 115°–120° as nearly as possible; then the temperature was raised to 124°. By continuous stirring the substance gradually became stiff. On cooling, it was treated in the same manner as in case of the resorcinol and orcinol compounds. Precipitated from its solution in sodium hydrate by hydrochloric acid it is a dirty-brown mass with which it was found impossible to deal satisfactorily.

DECOMPOSITION OF PARADIAZOORTHOTOLUENESULPHONIC ACID WITH ABSOLUTE METHYL ALCOHOL IN THE PRESENCE OF CERTAIN SUBSTANCES.

BY P. R. MOALE.[1]

Remsen and Dashiell,[2] working on the decomposition of paradiazoorthotoluenesulphonic acid under different conditions of temperature and pressure, found in the case of ethyl alcohol that both the hydrogen and the ethoxy reactions take place and that high pressure favors the ethoxy reaction and low pressure the hydrogen reaction; also that the decomposition itself is a function of temperature as well as of pressure, but left open the question as to which influenced the course of the reaction the more. Parks,[3] also working on the decomposition of the above diazo compound with methyl alcohol (absolute), found that the methoxy product only was formed at ordinary, increased, or diminished pressure, namely, paramethoxyorthotoluenesulphonic acid. Beeson[4] found that when diazobenzenesulphate or nitrate is decomposed with sodium methylate or ethylate, the hydrogen reaction takes place. At the suggestion of Professor Remsen, the decomposition of the above diazo compound with sodium methylate and ethylate was undertaken in the presence of absolute methyl and ethyl alcohols; also the decomposition with absolute methyl alcohol in the presence of ammonia, substituted ammonias, and potassium hydrate.

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[1] See Note to title of the preceding article.—I. R.

[2] This JOURNAL, **15**, 105.

[3] *Ibid*, **15**, 320.

[4] *Ibid*, **16**, 235.

Decomposition in Presence of Sodium Methylate.

The sodium methylate was made by dissolving a known weight of sodium in a definite volume of absolute methyl alcohol. Knowing the strength of the sodium methylate, the amount necessary for complete reaction with the diazo compound can be readily calculated. To the amount of sodium methylate required for 10 grams of the diazo compound some absolute methyl alcohol was added. The diazo compound was added gradually to the sodium methylate solution. Evolution of nitrogen took place. The temperature was kept down to about 20° during the reaction by a cooling-mixture, as the temperature rises rapidly on addition of the diazo compound. After the calculated amount of diazo compound had been added and nitrogen had ceased coming off, the liquid was evaporated to dryness on the water-bath. It was then finely powdered and treated with a slight excess of phosphorus pentachloride to form the chloride. The chloride was washed and then treated with concentrated ammonia. The product was crystallized from water and was obtained in fine white needles. It melted at 154°, which is the melting-point of orthotoluenesulphonamide. This shows that the hydrogen reaction did take place to some extent. The yield was small, but the reaction is interesting in that it shows that the presence of the alkali tends to cause the hydrogen reaction to take place to some extent, following in the line of Beeson's observations, while Parks found that with the absolute methyl alcohol alone only the methoxy product was formed. The residue left was a black tarry mass with which nothing satisfactory could be done.

Decomposition with Sodium Ethylate.

As before, 19 grams of the diazo compound were used and the method of decomposition was the same as in case of the sodium methylate. The action was the same as in case of the sodium methylate, though less vigorous. When placed in ice-water the reaction in the beaker stopped. Aldehyde was formed and was detected by its odor. On filtering, a considerable residue was left on the filter. It was a tarry mass from which nothing satisfactory could be obtained. The filtrate was evaporated to dryness. Neither from the residue or filtrate could orthotoluenesulphonamide be obtained. Both the residue and filtrate were reddish-black tarry substances and extremely difficult to work with.

Decomposition of the Diazo Compound with Absolute Ethyl Alcohol in the Presence of Potassium Hydrate.

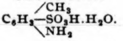
In this experiment no definite product was obtained. The action was less vigorous than that of the decomposition with sodium methylate or ethylate. The method of procedure was the same as before. After 10 grams of the diazo compound had been added to the calculated weight of potassium hydrate in a sufficient quantity of absolute ethyl alcohol to insure complete decomposition, the contents of the beaker were transferred to a pressure-flask and gently heated. Some decomposition took place at 700 mm. pressure. In about an hour the alcohol boiled quietly, all gas having stopped coming off. The solution was dark-red. On filtering, a black carbonaceous mass was left on the filter. From the filtrate, by evaporation and drying, a reddish mass was obtained which turned to a black gummy mass in the air. Estimations of sulphur and potassium showed that the products were mixtures.

Decomposition of the Diazo Compound with Absolute Methyl Alcohol Saturated with Dry Ammonia Gas.

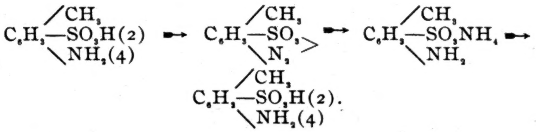
To the requisite amount of methyl alcohol (absolute) saturated with dry ammonia gas, absolute methyl alcohol was added. To this was gradually added 10 grams of diazo compound. Reaction took place at ordinary temperature. After the reaction was over, the liquid was evaporated to dryness on the water-bath. The substance was finely powdered, and by treatment successively with phosphorus pentachloride and concentrated ammonia the amide was formed. The amide, after crystallization from water, melted at 164°, which is the melting-point of the amide of paratoluidineorthosulphonic acid, from which acid the diazo compound had been made. For further confirmation the dried product was treated with concentrated hydrochloric acid to convert it into the free acid. The solution was evaporated down on the water-bath and then allowed to crystallize, filtered, and washed well. The acid is insoluble in cold water. Recrystallized from boiling water, it comes down in glistening rhombohedral plates. Analysis gave the following results:

I. 0.0834 gram of substance gave 0.0954 gram of $BaSO_4$ (Liebig method).

II. 0.1106 gram of substance gave 0.1290 gram of $BaSO_4$ (Liebig method).

	Calculated for  $C_6H_3\begin{cases}CH_3\\SO_3H.H_2O\\NH_2\end{cases}$	Found. I.	Found. II.
S	15.61	15.72	16.02

Griffin,[1] working in this laboratory, has shown that in the case of the decomposition of the diazo compound of paratoluidinemetasulphonic acid with absolute methyl alcohol saturated with dry ammonia gas a similar reaction takes place. The course of the transformation is expressed thus:



$$C_6H_3\begin{cases}CH_3\\SO_3H(2)\\NH_2(4)\end{cases} \rightarrow C_6H_3\begin{cases}CH_3\\SO_3\\N_2\end{cases}\!\!> \rightarrow C_6H_3\begin{cases}CH_3\\SO_3NH_4\\NH_2\end{cases} \rightarrow C_6H_3\begin{cases}CH_3\\SO_3H(2).\\NH_2(4)\end{cases}$$

The specimen of the diazo compound used was tested for undiazotized paratoluidineorthosulphonic acid and none was found.

Decomposition with Absolute Methyl Alcohol and Aniline.

Having shown that paradiazoorthotoluenesulphonic acid was converted back to the paratoluidineorthosulphonic acid by absolute methyl alcohol and ammonia, it was thought desirable to try the action of substituted ammonias, and aniline was used. As before, each specimen of diazo compound was tested for undiazotized acid. In no case was any appreciable quantity of free acid found. In this case three reactions take place, according to the proportions of aniline and methyl alcohol used, one common product and apparently three or four different dye-stuffs being formed. A fourth reaction takes place on gentle heating, with no evolution of gas, a dye-stuff being formed.[1]

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[1] This Journal, 19, 171.

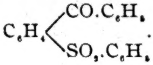
PARABENZOYLDIPHENYLSULPHONE

AND RELATED COMPOUNDS.[2]

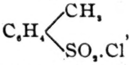
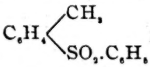
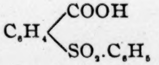
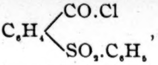
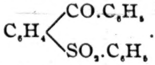
BY LYMAN C. NEWELL.

Introduction.

The primary object in mind when this research was begun was to make and study orthobenzoyldiphenylsulphone



$$C_6H_4\Big\langle\begin{array}{l}CO.C_6H_5\\SO_2.C_6H_5\end{array}.$$

This compound was obtained by Remsen and Saunders[3] by the action of benzene and aluminium chloride on the mixed chlorides and on the symmetrical chloride of orthosulphobenzoic acid. The general plan was to start with toluenesulphonechloride,  $C_6H_4\Big\langle\begin{array}{l}CH_3\\SO_2.Cl\end{array}$, replace the chlorine by the phenyl group by the Friedel-Crafts reaction, thus passing to tolylphenylsulphone,  $C_6H_4\Big\langle\begin{array}{l}CH_3\\SO_2.C_6H_5\end{array}$; oxidize the methyl group, and thus make phenylsulphonebenzoic acid,  $C_6H_4\left\langle\begin{matrix}COOH\\SO_2.C_6H_5\end{matrix}\right.$; then treat this acid or its salt with phosphorus pentachloride to form the corresponding acid chloride,  $C_6H_4\left\langle\begin{matrix}CO.Cl\\SO_2.C_6H_5\end{matrix}\right.$, which, by the action of benzene and aluminium chloride, would yield benzoyldiphenylsulphone,  $C_6H_4\left\langle\begin{matrix}CO.C_6H_5\\SO_2.C_6H_5\end{matrix}\right.$.

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[1] Although Mr. Moale did a good deal of work on these reactions, it was not possible for him to carry the work to completion on account of a lack of time. It was taken up later by Mr. Hollis, and the results reached by him will be published later.—I. R.

[2] From the Author's Dissertation, submitted to the Board of University Studies of the Johns Hopkins University for the degree of Doctor of Philosophy, June, 1895. The work was undertaken at the suggestion of Professor Remsen, and carried on under his guidance.

[3] This JOURNAL, 17, 362.

It was deemed advisable to begin the work in the *para* series, and, as the results have been so fruitful, nearly the whole investigation has been confined to this series.

Preparation of Material.

The starting-point of this investigation was paratoluenesulphone chloride. The actual substance used was prepared by the usual method, and was a kilogram of the chloride which had accumulated as a residue in the preparation of the ortho analogue. The raw product was washed with cold water, pumped out on the filter-pump to remove all traces of the liquid ortho chloride, dried, and recrystallized from ether.

Paratolylphenylsulphone.

This compound was made by Michael and Adair,[1] in 1878, from benzenesulphonic acid, toluene and phosphorus pentoxide, and also from toluenesulphonic acid, benzene and phosphorus pentoxide; it was made in the same year by Beckurts and R. Otto[2] by the action of toluene and aluminium chloride on benzenesulphone chloride; and by R. Otto,[3] in 1885, from toluenesulphone chloride, benzene, and mercury diphenyl. The products obtained by these different methods melted at 124°–125°, and were either fine white prisms or small rhombohedral plates.

The method employed in this investigation was analogous to that of Beckurts and R. Otto,[4] the only difference being the use of paratoluenesulphone chloride, which was trans-

[1] Ber. d. chem. Ges., 11, 116.

[2] *Ibid*, 11, 2068.

[3] *Ibid*, 18, 249.

[4] *Loc. cit.*

formed into paratolylphenylsulphone by *benzene* and aluminium chloride, *i. e.*, by the Friedel-Crafts reaction. The detailed method is as follows: One part paratoluenesulphone chloride is dissolved in an equal weight of warm benzene, and the solution poured into a flask of convenient size, which is attached to a return-condenser. The flask is then placed in a water-bath, the temperature of the water raised to about 75°, and powdered aluminium chloride introduced into the flask in small portions until an amount has been added which is equal to three-fourths the weight of the benzene used. The reaction proceeds briskly at 75° until the chloride is almost entirely converted into the sulphone. When the evolution of hydrochloric acid has ceased, the temperature is raised to 80°, and kept at this point for three-quarters of an hour. The product of the reaction, which is a black, viscous mass, is poured into a large volume of warm water, acidified with hydrochloric acid and warmed on the water-bath till all the benzene is driven off. The paratolylphenylsulphone then appears on the surface of the water as small brownish-yellow lumps. It is filtered, washed with warm water, purified by animal charcoal, and crystallized from hot, ordinary alcohol. The purified product has the form of hexagonal plates, and melts at 124°-125°. The yield is about ninety-five per cent. of the theoretical amount.

Paraphenylsulphonebenzoic Acid.

This acid was also made by Michael and Adair[1] by oxidizing paratolylphenylsulphone with the calculated amount of potassium permanganate in acetic acid solution, and by boiling the sulphone with potassium permanganate dissolved in a large excess of water. The yield in each case was exceedingly small. The product obtained by both methods crystallized from hot alcohol in fine transparent prisms, which were said to melt above 300°.

The methods employed by Michael and Adair were tried and abandoned, because the yield was small and the methods tedious. The sulphone was also boiled several hours with a mixture of sulphuric acid and potassium dichromate, but this method proved unsuccessful. The following method was finally adopted : Five parts of the sulphone are dissolved in the smallest possible quantity of warm glacial acetic acid in a flask which is attached to a return-condenser. The solution is raised nearly to the boiling-point, and 8 parts of chromic acid, also dissolved in the least possible amount of cold glacial acetic acid, are added through the inner tube of the condenser in portions of about 10 cc. each. After each addition of the chromic acid solution, the flask is shaken, the temperature being regulated so that the solution just boils. When all the chromic acid has been added, the mixture is boiled for two hours ; the excess of acetic acid is then distilled off, and when the flask has cooled, the paraphenylsulphonebenzoic acid remains as a fine powder, more or less greenish in color. The contents of the flask are poured into a large porcelain dish and washed several times with hot water. It is better to wash by decantation until only a slight greenish tinge remains, and then wash with the aid of the filter-pump, otherwise a trace of chromium salts will persist in remaining in the crystallized product. The acid is then converted into the sodium salt by boiling with sodium carbonate, and the acid precipitated by hydrochloric acid.

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[1] *Loc. cit.*

The acid prepared in this way has, when wet, the appearance of whipped cream, and when dry is a pure white powder. It is soluble in boiling nitrobenzene, and separates out as a crystalline mass ; it is soluble in hot glacial acetic acid, from which it crystallizes in small, transparent, double wedge-shaped prisms. Both these solvents are difficult to remove from the crystallized product. It is insoluble in absolute ether and in both hot and cold water. The best solvent is hot alcohol (95 per cent.), from which it crystallizes easily in small, white prisms. Michael and Adair[1] state that the acid melts above 300°. This is incorrect, as several determinations of the melting-point of the crystallized product show conclusively that paraphenylsulphonebenzoic acid melts at 273° uncorr.

Calcium Salt.—Fine white needles separate out of the cooled aqueous solution, which are slightly deliquescent in the air. The following results were obtained on analysis :

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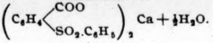
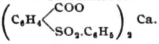
[1] *Loc. cit.*

0.2346 gram of the salt heated at 155° to constant weight lost 0.0041 gram of H_2O.

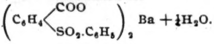
	Calculated for  $\left(C_6H_4{<}^{COO}_{SO_2.C_6H_5}\right)_2 Ca + \frac{1}{2}H_2O$.	Found.
H_2O	1.58	1.74

0.2305 gram dehydrated salt gave 0.0561 gram $CaSO_4$.

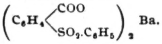
	Calculated for  $\left(C_6H_4{<}^{COO}_{SO_2.C_6H_5}\right)_2 Ca$.	Found.
Ca	7.11	7.15

Barium Salt.—This crystallizes from the cooled aqueous solution in fine white needles, which show a marked tendency to arrange themselves in sheaves. Analysis gave the following results :

0.2715 gram air-dried salt when heated at 110° to constant weight lost 0.002 gram H_2O.

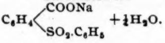
	Calculated for  $\left(C_6H_4{<}^{COO}_{SO_2.C_6H_5}\right)_2 Ba + \frac{1}{4}H_2O$.	Found.
H_2O	0.68	0.73

0.2242 gram dehydrated salt gave 0.0784 gram $BaSO_4$.

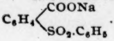
	Calculated for  $\left(C_6H_4{<}^{COO}_{SO_2.C_6H_5}\right)_2 Ba$.	Found.
Ba	20.81	20.57

Sodium Salt.—This salt crystallizes from alcohol in fine needles, and resembles the barium salt in its tendency to form sheaf-like clusters. It is slightly efflorescent in the air. The following results were obtained on analysis :

0.1711 gram of the salt dried between filter-paper and heated at 110° to constant weight lost 0.0018 gram H_2O.

	Calculated for  $C_6H_4{<}^{COONa}_{SO_2.C_6H_5} + \frac{1}{4}H_2O$.	Found.
H_2O	1.58	1.05

0.1693 gram dehydrated salt gave 0.0414 gram Na_2SO_4.

	Calculated for  $C_6H_4\begin{cases}COONa\\SO_2.C_6H_5\end{cases}$	Found.
Na	8.11	7.93

Paraphenylsulphonebenzoyl Chloride.

This compound can be made by heating paraphenylsulphonebenzoic acid or its salts with phosphorus pentachloride. It is best prepared from the acid. Equal weights of the powdered acid and dry phosphorus pentachloride are intimately mixed in a flask. To this flask is attached a glass tube about 45 cm. long and having two arms of different lengths bent at angles of 110° to the horizontal part of the tube; the shorter arm passes just through the stopper of the flask, while the longer arm reaches to the bottom of a test-tube surrounded with ice. The flask is placed in a sulphuric-acid bath, slowly heated to 200° and kept at this temperature for about half an hour. If the operation is conducted slowly, this process changes all the acid into the corresponding acid chloride, and most of the phosphorus oxychloride distils over into the test-tube. Hydrochloric acid is evolved during almost the whole process. When the operation is over the flask is removed from the bath and allowed to cool. The chloride solidifies at 145°–150° to a brownish amorphous mass. It is softened with a little warm water, transferred from the flask to a mortar, powdered and washed with warm water by decantation. This operation must be repeated several times, otherwise the chloride will retain traces of phosphorus oxychloride, which it is difficult to remove from the crystallized product. The chloride is carefully dried and crystallized from hot petroleum ether (boiling-point 80°–110°). It is not easily soluble in boiling petroleum ether, but the liquid boiling between these points was found to be the best of several solvents. The yield is about 90 per cent. of the theoretical.

The chloride crystallizes from boiling petroleum ether in fine, glistening, white plates and sometimes in short, white needles, depending upon the method of extraction and rate of crystallization. It is soluble in warm, dry benzene, from which it crystallizes in small rhombohedrons, if the liquid is slowly evaporated. It is soluble in boiling absolute ether and crystallizes from this solvent in delicate needles. It is insoluble in petroleum ether boiling between 30° and 50°. The melting-point was found by a Zincke thermometer to be 145.2°–145.8°.

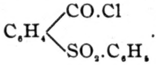
When the chloride is boiled with water the corresponding acid is regenerated and hydrochloric acid is formed. A determinaton of chlorine by this method gave the following result:

0.1697 gram chloride gave 0.0845 gram AgCl.

	Calculated for $C_{13}H_9SO_3Cl$.	Found.
Cl	12.62	12.31

The chlorine was also determined by the following method: The chloride was heated just to the boiling-point for several hours with a dilute solution of caustic potash and then acidified with dilute nitric acid; the regenerated acid is filtered off and the chlorine precipitated as usual. By this method 12.42 per cent. of chlorine was found.

The chloride is slightly volatile. When 0.0505 gram of the air-dried substance was slowly heated to 137° it lost 0.0043 gram. In accordance with the analysis, general conduct, and method of preparation, this chloride has the formula



$$C_6H_4\left\langle\begin{array}{l}CO.Cl\\SO_2.C_6H_5\end{array}\right.$$.

Paraphenylsulphonebenzamide.—When paraphenylsulphonebenzoyl chloride is treated with an excess of concentrated ammonium hydroxide at the ordinary temperature, and allowed to stand twenty-four hours with occasional stirring, there is no visible change, since both the chloride and the product of the reaction are insoluble in the liquid used. The white powder which finally settles to the bottom of the beaker has much the same appearance as the chloride, but it is insoluble in boiling petroleum ether (boiling-point 80–110°) and also in hot anhydrous ether. From hot alcohol (95 per cent.) it separates out in small transparent acicular crystals, which melt at 242°–243° (uncorr.).

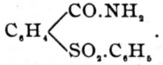
Analysis for nitrogen by the absolute method and for sulphur by Liebig's method gave the following results:

I. 0.3743 gram substance gave 16.44 cc. = 0.0206 gram nitrogen under standard conditions.

II. 0.3545 gram substance gave 0.3212 gram $BaSO_4$.

	Calculated for $C_{13}H_{11}SO_3N$.	Found. I.	II.
N	5.37	5.55	....
S	12.27	....	12.45

The filtrate from the above method of preparation, when evaporated to dryness, gave nothing but ammonium chloride. The method of preparation together with the analysis show this compound to be the amide corresponding to paraphenylsulphonebenzoyl chloride,



$$C_6H_4\begin{cases}CO.NH_2\\SO_2.C_6H_5\end{cases}.$$

Paraphenylsulphonebenzanilide.—This anilide is best made in the following manner: Paraphenylsulphonebenzoyl chloride is dissolved in warm dry benzene contained in an Erlenmeyer flask, and an excess of aniline added, drop by drop, with constant shaking. When all the aniline has been added and the mixture shaken for about ten minutes, cold water is added to dissolve the aniline hydrochloride. At this stage the aniline appears as a white gummy mass floating on the surface of the liquid. The mixture is filtered and the anilide washed with warm benzene and finally with cold alcohol. The filtrate, on evaporation to dryness, proved to contain nothing but aniline hydrochloride.

The anilide is soluble in hot alcohol (95 per cent.), but insoluble in boiling petroleum ether (boiling-point 80°–110°), in hot absolute alcohol, boiling caustic soda, and boiling hydrochloric acid. It crystallizes from alcohol in transparent small prisms which melt at 202°–203° (uncorr.).

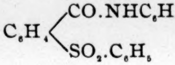
Analyses made by the same methods as in the case of the amide (*supra*) gave the following results:

I. 0.2904 gram substance gave 10.43 cc. = 0.01308 gram nitrogen under standard conditions.

II. 0.3073 gram substance gave 0.213 gram $BaSO_4$.

	Calculated for $C_{19}H_{15}SO_3N$.	Found. I.	II.
N	4.16	4.50	....
S	9.48	....	9.52

The method of preparation and analysis show that this compound is the anilide of paraphenylsulphonebenzoic acid, and hence has the formula



$$C_6H_4\left\langle\begin{array}{l}CO.NHC_6H_5\\SO_2.C_6H_5\end{array}\right. .$$

Parabenzoyldiphenylsulphone.

The detailed method used in the preparation of this compound is as follows: Ten grams of the chloride is dissolved in twice its weight of warm benzene in a small beaker. When the temperature is 70°–75°, from 12 to 15 grams of powdered aluminium chloride is added in three portions; if the action is too vigorous the liquid is allowed to cool below 70°, when the reaction almost ceases. As the operation proceeds, hydrochloric acid is evolved and the product of the reaction settles to the bottom of the beaker as a dark-red oily liquid. The transformation is complete when no more hydrochloric acid is evolved on raising the temperature to the boiling-point of the benzene, the whole operation requiring not more than fifteen minutes. The contents of the vessel were poured into a large volume of water and acidified with hydrochloric acid. The reddish oil solidified to a yellowish-brown, flocculent mass, which encrusted the surface of the liquid after the last traces of benzene had been driven off on the water-bath. It was then washed free from acid with warm water, and crystallized from alcohol (95 per cent.), the yield being about 90 per cent.

The substance crystallizes from alcohol in fine, white, lustrous needles, which, when dry, pack together like felt. They require only one purification with animal charcoal, and, when pure, melt sharply at 133° (uncorr.). They are slightly soluble in cold and warm benzene, in warm ether, and very soluble in warm alcohol. They dissolve in warm concentrated nitric acid and in cold, concentrated sulphuric acid, and are recovered unchanged from both. They are not attacked by alcoholic potash even when the substances are boiled together for a day; and they are stable in the air.

The following results were obtained on analysis:

I. 0.1504 gram gave 0.3851 gram CO_2, and 0.6375 gram H_2O.
II. 0.2257 gram gave 0.1524 gram $BaSO_4$.
III. 0.1310 gram gave 0.0908 gram $BaSO_4$.
IV. 0.2797 gram gave 0.2088 gram $BaSO_4$.

	Calculated for $C_{19}H_{14}SO_3$.	Found. I.	II.	III.	IV.
C	70.78	70.37	....	....	....
H	4.35	4.70	....	....	....
S	9.95	....	9.37	9.53	10.26

The determinations of carbon and hydrogen were made by de Roode's modification of the lead chromate method; the first two determinations of sulphur were made by Liebig's method, and the last by the method of Carius.

When orthobenzoyldiphenylsulphone is heated slowly with an excess of caustic potash "the action takes place rapidly at 200°–210°, with formation of a yellowish-brown mass. This, when warmed with water, partially dissolves; the residue when separated by filtration and recrystallization from alcohol, gives the characteristic rhombic crystals of diphenylsulphone, melting at 123°–124°, and having the solubility and general properties of that compound. The filtrate treated with hydrochloric acid gives a precipitate of benzoic acid."[1]

When parabenzoyldiphenylsulphone is subjected to the same treatment, the results are entirely different. The sulphone was fused twice in a silver crucible, four times in a sealed hard-glass tube, and once in a distilling-bulb. In all cases the general character of the reaction is the same. Incipient fusion produces a greenish scum on the surface of the molten potash, and at the same time a volatile substance is given off having a pleasant ethereal odor.[2] Attempts were made to obtain the substance giving this odor but they were unsuccessful. When the temperature reaches about 200°–210°, the greenish scum turns to a yellowish-brown porous mass, which still remains on the surface of the potash. When the fused mass is treated as in the fusion of the ortho compound, there are no traces of either diphenylsulphone or benzoic acid. A variety of results were obtained, even when the fusion was apparently conducted in precisely the same manner. In one instance a substance was obtained which had some properties characteristic of benzoic acid, but it was impure and the quantity was so small that it could not be regarded as a real product of the reaction. In two instances a substance was obtained melting at 126°–128° and crystallizing from hot alcohol (95 per cent.) in small transparent flakes, but the amount was too small for identification. In several of the fusions—especially those performed in the sealed glass tube—a white powder was obtained from an alcoholic solution of that portion of the fused mass insoluble in water. This powder melted at about 90°, but was impure and was not further investigated.

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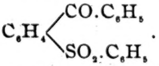
[1] Remsen and Saunders, *Loc. cit.*

[2] This volatilization may be an explanation of the low results obtained in the sulphur determinations by Liebig's method.

In view of these facts it must be concluded that when parabenzoyldiphenylsulphone is fused with caustic potash, it does not decompose into benzoic acid and diphenylsulphone, differing markedly in this respect from the corresponding ortho compound.

Derivatives of Parabenzoyldiphenylsulphone.

The method of preparation, the properties, and analysis of this compound show that it must have the structural formula



$$C_6H_4\left\langle\begin{array}{l}CO.C_6H_5\\SO_2.C_6H_5\end{array}\right.$$

. This being the fact, we should naturally expect it to yield a hydrazone with phenylhydrazine, and an oxime, or oximes, with hydroxylamine, owing to the presence of the carbonyl group, CO, in the compound. Both the hydrazone and the oxime were made.

Hydrazone.—When equal quantities of parabenzoyldiphenylsulphone and phenylhydrazine, dissolved in a convenient quantity of alcohol, are boiled on the water-bath with a return-condenser for three days, lemon-yellow, lustrous needles separate out of the cooled alcohol. These needles when washed free from phenylhydrazine and recrystallized from hot alcohol (95 per cent.) melt sharply at 184° (uncorr.). When boiled for a day with concentrated hydrochloric acid, the substance splits up into phenylhydrazine and the original substance. The beautiful yellow color is not removed by animal charcoal, and the substance is stable in the air.

Analysis gave the following results:

I. 0.0518 gram gave 0.0288 gram $BaSO_4$.

II. 0.18775 gram gave 0.496 gram CO_2, and 0.0802 gram H_2O.

III. 0.1953 gram gave 0.5191 gram CO_2, and 0.0970 gram H_2O.

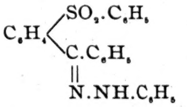
IV. 0.1873 gram gave 0.4943 gram CO_2, and 0.0844 gram H_2O.

V. 0.1420 gram gave 8.05 cc. = 0.01009 gram nitrogen under standard conditions.

	Calculated for $C_{25}H_{20}SO_2N_2$.	Found.				
		I.	II.	III.	IV.	V.
S	7.77	7.64	....	....	....	....
C	72.78	....	72.04	72.48	72.00	....
H	4.86	....	4.75	5.52	5.00	....
N	6.83	....	....	....	....	7.11

The sulphur was determined by the method of Carius, the nitrogen by the absolute method, and the carbon and hydrogen by de Roode's modification of the lead chromate method.

The preparation, general conduct, and analysis of this compound show it to be paradiphenylsulphonebenzoylhydrazone. Its structural formula is probably:



$$C_6H_4\begin{cases}SO_2.C_6H_5\\ C.C_6H_5\\ \quad\|\\ N.NH.C_6H_5\end{cases}$$

The alcoholic filtrate obtained in the preparation of the first specimens of this hydrazone was evaporated to dryness, and in each case a reddish crystalline mass resulted. This residue was at first thought to be the hydrazone itself. It proved however to be something entirely different. It was soluble in hot water, cold methyl alcohol, hot ordinary ether, and in boiling petroleum ether (boiling-point 80°–110°). Its color when crystallized was a faint yellow and was not removed by animal charcoal. By crystallization from different solvents two kinds of crystals were obtained—small plates and needles both melting at 125°-127°. Both kinds of crystals were split up into phenylhydrazine and acetic acid in the following manner: The crystals were boiled with concentrated hydrochloric acid for a day, and into this solution, made alkaline with caustic potash, steam was passed; an oil distilled over with the steam, which had the odor of phenylhydrazine and reduced Fehling's solution. The alkaline liquid into which the steam was passed was evaporated to dryness, and in the residue acetic acid was detected by the ethyl acetate test.

The properties and reactions of this substance—particularly its decomposition into phenylhydrazine and acetic acid—suggested its identity with acetylphenylhydrazine. A sample of pure acetylphenylhydrazine was made according to the method of Fischer.[1] It melted at 128° and had all the properties of the residue mentioned above, including solubility, crystal forms, reducing power, etc. It also was decomposed by the method mentioned above into acetic acid and phenylhydrazine. There seems to be little doubt that the substance in question was acetylphenylhydrazine. The evidence, however, is not conclusive. The substance was not obtained in every instance, in fact only in the first two or three experiments, and then not in very large quantities. Not enough was obtained in a condition pure enough for analysis. While it seems plausible that from some deep-seated cause the alcohol used in the experiment may have been oxidized to acetic acid, and that the acetic acid may have formed acetylphenylhydrazine with the excess of phenylhydrazine present, still the conclusion must be drawn that if acetylphenylhydrazine is formed as a secondary product when parabenzoyldiphenylsulphone is treated with phenylhydrazine in alcoholic solution, it is formed only as the result of some unknown and perhaps accidental cause.

Oxime.—The oxime corresponding to parabenzoyldiphenylsulphone was first made by boiling an alcoholic solution of the sulphone with a slight excess of an aqueous solution of hydroxylamine hydrochloride to which the calculated amount of sodium carbonate had been added. It was found necessary to continue the action for three days in order to transform all the sulphone into the oxime. By this method a mixture was obtained which by repeated crystallizations from hot alcohol (95 per cent.) finally yielded thin, irregular leaflets melting at 201° (uncorr.), with evolution of a gas, and small white needles melting at 154° (uncorr.). This method was abandoned for one similar to that used by Auwers[1] for the preparation of the benziloximes. The method finally adopted is as follows: Eleven parts of parabenzoyldiphenylsulphone are dissolved in a slight excess of hot ordinary alcohol, and to this hot solution there is added a clear aqueous solution of 5 parts of hydroxylamine hydrochloride. If the solution is not clear, alcohol is added until the hot solution is perfectly clear. To this solution there is added a filtered aqueous solution of 8 parts of caustic soda. The clear liquid is now boiled for not less than two hours on the water-bath, filtered, if necessary, while hot, and acidified with hydrochloric acid. The oxime which settles out as a white powder is filtered, washed with cold water, dried at 110°, and recrystallized from hot alcohol (95 per cent). The crystals obtained by this method are always the thin, irregular leaflets melting at 201° (uncorr.). When boiled for a day with concentrated hydrochloric acid they split up into hydroxylamine and the original substance. They are insoluble in cold water, and the best crystals come from hot alcohol.

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[1] Ann. Chem. (Liebig), **190**, 129.

Analysis gave the following results:

I. 0.1986 gram gave 0.4872 gram CO_2, and 0.083 gram H_2O.

II. 0.1987 gram gave 0.4857 gram CO_2, and 0.0809 gram H_2O.

III. 0.1608 gram gave 0.1208 gram $BaSO_4$.

IV. 0.2393 gram gave 8.22 cc. = 0.0103 gram nitrogen under standard conditions.

	Calculated for $C_{18}H_{15}SO_3N$.	Found. I.	II.	III.	IV.
C	67.63	66.92	66.97	....	....
H	4.46	4.64	4.48	....	....
S	9.55	....	....	9.70	....
N	4.16	....	....	....	4.33

The determinations were made by the same methods as in the analysis of the hydrazone.

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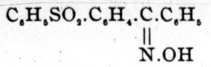
[1] Ber. d. chem. Ges., **22**, 604.

The preparation, general conduct, and analysis of this compound leave no doubt that it is an oxime of parabenzoyldiphenylsulphone and has one of the two structural formulas represented thus :

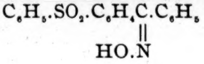
I.



$$C_6H_5SO_2.C_6H_4.\underset{\underset{N.OH}{\|}}{C}.C_6H_5$$

or

II.



$$C_6H_5.SO_2.C_6H_4\underset{\underset{HO.N}{\|}}{C}.C_6H_5$$

The needles melting at 154° (see above) were obtained only once, and then by the first method of preparation. The conditions under which they were made were reproduced as far as possible, since they were thought to be an isomeric modification of the oxime isolated, but to no avail. The conditions and methods were also modified in various ways, but no trace of an isomer could be obtained after many trials. The work on this possible isomeric form was abandoned on account of lack of material.

The comparative ease with which the oxime and hydrazone of parabenzoyldiphenylsulphone are made, together with the fact that the methods of preparation vary somewhat from those used by Remsen and Saunders in this ineffectual attempt to prepare the oxime and the hydrazone of *ortho*benzoyldiphenylsulphone, suggested the possibility of obtaining a reaction by the methods used in the case of the para compound. Accordingly, some orthobenzoyldiphenylsulphone was purified and recrystallized till it had a constant melting-point (187° uncorr.). It was then boiled with an equal weight of phenylhydrazine in alcoholic solution. At the end of three days the original substance was recovered. At the end of the five days' continuous boiling the orthobenzoyldiphenylsulphone crystallized out of the cooled alcohol. The alcoholic filtrate was evaporated nearly to dryness, and yielded nothing but phenylhydrazine.

Another portion of the orthosulphone was boiled in alcoholic solution with the proper proportions of hydroxylamine hydrochloride and caustic soda under the same conditions as those used for the preparation of the oxime of the parasulphone. At the end of two hours' boiling the original substance settled out; the action was continued for nine and a half hours and at the end of that time the orthobenzoyldiphenylsulphone crystallized out of the solution when cooled. It had the same crystal form and the same melting-point as the original substance used. These experiments confirm the work of Remsen and Saunders, who obtained neither the oxime nor the hydrazone.

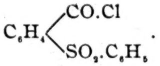
Summary.

The results of this investigation may be briefly summarized as follows:

1. Paratoluenesulphone chloride, by means of the Friedel-Crafts reaction, passes easily into paratolylphenylsulphone.

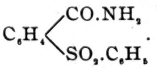
2. This sulphone can be best oxidized by chromic acid to paraphenylsulphonebenzoic acid, which forms well characterized salts.

3. When heated to 200° (under proper conditions) with phosphorus pentachloride, this acid forms an acid chloride having the formula



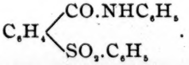
$$C_6H_4\left\langle\begin{array}{l}CO.Cl\\SO_2.C_6H_5\end{array}\right. .$$

4. Paraphenylsulphonebenzoyl chloride when treated with concentrated ammonium hydroxide at the ordinary temperature, forms an amide having the constitution



$$C_6H_4\left\langle\begin{array}{l}CO.NH_2\\SO_2.C_6H_5\end{array}\right. .$$

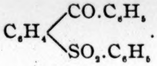
And when treated with an excess of aniline in benzene solution, it yields an anilide of the formula



$$C_6H_4\left\langle\begin{array}{l}CO.NHC_6H_5\\SO_2.C_6H_5\end{array}\right. .$$

5. A third compound was obtained from paraphenylsulphonebenzoyl chloride, by means of the Friedel-Crafts reaction, which proved to be parabenzoyldiphenylsulphone, a compound analogous to the compound obtained by Remsen and Saunders

from the chlorides of orthosulphobenzoic acid by the same reaction. It has the constitutional formula



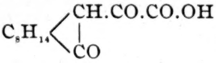
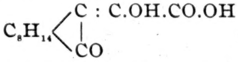
$$C_6H_4\left\langle\begin{array}{l}CO.C_6H_5\\SO_2.C_6H_5\end{array}\right..$$

6. This compound, unlike the corresponding ortho compound, is not decomposed into benzoic acid and diphenylsulphone when fused with caustic potash. On the other hand, it does yield a hydrazone and an oxime.

THE ACTION OF ETHYLIC OXALATE ON CAMPHOR (III).

By J. Bishop Tingle.

THEORETICAL.

In the previous papers[1] the preparation of camphoroxalic acid was described, and the formation by it of an additive compound with hydroxylamine, a fact which is not in harmony with the keto formula,  $C_8H_{14}\left\langle\begin{array}{l}CH.CO.CO.OH\\|\\CO\end{array}\right.$, but is easily explicable if the substance is regarded as an unsaturated hydroxy-derivative,  $C_8H_{14}\left\langle\begin{array}{l}C : C.OH.CO.OH\\|\\CO\end{array}\right.$. Subsequently C. Harries and F. Lehmann[2] have shown that hydroxylamine and phorone interact in a similar manner; in fact, the reaction appears to be a general one for unsaturated ketones, RCH : CH.COR, to which class camphoroxalic acid belongs. The work described in the following pages was undertaken in the hope of throwing further light on the subject. By the action of acetic anhydride on camphoroxalic acid, three substances are formed melting at 242°, 190°, and 118°, respectively. The yields in all cases were poor, in spite of numerous alterations in the experimental conditions. At present it is impossible to say anything as to the nature of the first compound (m. p. 242°); the second (m. p. 190°) is probably an anhydride, as it is formed by the action of benzoyl chloride on camphoroxalic acid. The third compound (m. p. 118°) proved to be a monacetyl derivative,

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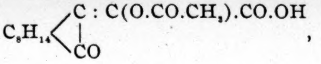
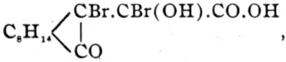
[1] This Journal, **19**, (1897) 393; J. Chem. Soc., **57**, (1890) 652.

[2] Ber. d. chem. Ges., **30**, 231, 2726.

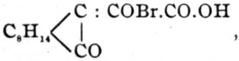


$$\mathrm{C_8H_{14}}\left\langle\begin{array}{l}\mathrm{C : C(O.CO.CH_3).CO.OH}\\ |\\ \mathrm{CO}\end{array}\right.,$$

and is also formed by the action of acetic anhydride on ethylic camphoroxalate. The acetyl derivative readily combines with bromine vapor; the product is oily, quickly evolves hydrogen bromide at the ordinary temperature, and the residue could not be induced to crystallize. By the action of bromine vapor on camphoroxalic acid an oily compound is obtained, which crystallizes with difficulty, and could not be completely freed from oxalic acid. When the acid is treated with bromine in chloroform solution, evolution of hydrogen bromide commences immediately. As the product consisted of an oil it was reduced with magnesium amalgam. The substance thus obtained closely resembles camphoroxalic acid in general properties, but an examination of the crystals shows that it is not identical with this, and it will be more fully investigated subsequently. The action of bromine may take place in two ways, according to whether the initial addition occurs in the side-chain or in the camphor nucleus. In the former case, the additive compound would be represented by the formula

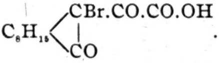


$\mathrm{C_8H_{14}}\left\langle\begin{array}{l}\mathrm{CBr.CBr(OH).CO.OH}\\ |\\ \mathrm{CO}\end{array}\right.$, and would produce, by the elimination of hydrogen bromide, the compound



$$\mathrm{C_8H_{14}}\left\langle\begin{array}{l}\mathrm{C : COBr.CO.OH}\\ |\\ \mathrm{CO}\end{array}\right.,$$

or



$$\mathrm{C_8H_{15}}\left\langle\begin{array}{l}\mathrm{CBr.CO.CO.OH}\\ |\\ \mathrm{CO}\end{array}\right..$$

The reduction of the latter compound would then yield a diketonic acid, isomeric with camphoroxalic acid. The fact that the bromo-additive compound gives no coloration with ferric chloride, whilst the substance produced after the elimination of hydrogen bromide does so, supports this view, as does also the readiness with which addition of bromine to camphoroxalic acid takes place. On the other hand it is known that camphor very readily combines with bromine to form a dibromide $C_{10}H_{16}OBr_2$, which easily eliminates hydrogen bromide, and is converted into bromocamphor $C_{10}H_{15}BrO$; this, when reduced, should give, without difficulty, an isomeric camphoroxalic acid, the isomerism being due to a difference in the camphor nucleus. It might be expected too that the negative nature of the carboxyl group would be likely to hinder the addition of bromine to the ethylene linkage in the side-chain. The reduced bromide crystallizes in six-sided plates apparently belonging to the monoclinic system; it melts at 84°–84.5°, and gives a red coloration with ferric chloride; camphoroxalic acid melts at 88°.

The compound formed by the action of benzoyl chloride on camphoroxalic acid has been referred to above; with benzoic anhydride little or no reaction takes place below 150°; at this temperature carbonic anhydride is evolved, and no definite product could be isolated.

When quickly distilled under the ordinary pressure, camphoroxalic acid yields some camphor, but a considerable proportion passes over unchanged. Heating with barium hydroxide, in a current of dry purified hydrogen, causes almost complete conversion into camphor and oxalic acid, indicating its hydrolysis at the position of the ethylene linkage. Attempts to convert camphoroxalic acid into an isomeric acid, by prolonged heating at 150°, were unsuccessful, whilst partial etherification with alcoholic hydrogen chloride failed to show any indication of nonhomogeneity.

When boiled with phenylhydrazine, in anhydrous ether free from alcohol, camphoroxalic acid yields a crystalline salt, which melts and evolves gas at 214°–215°.

By the action of dilute sulphuric acid (1 : 3) on camphoroxalic acid, at 135°, during three hours, oxalic acid is produced in small quantity, but the larger portion is converted into a new acid, $C_{12}H_{20}O_6$, which crystallizes with some difficulty in granular nodules melting at 92°–93°. It is distinguished from camphoroxalic acid by its sparing solubility in ligroïn, by the production of a deep-blue coloration with alcohol and ferric chloride, and by its failure to yield a sparingly soluble calcium salt. Analysis shows that it is formed by the addition of 2 molecules of water to camphoroxalic acid.

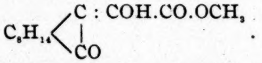
Camphoroxalic acid has been examined crystallographically and belongs to the hexagonal system.

The only specimens of ethylic camphoroxalate hitherto described were mixed with varying quantities of ethylic oxalate ; the pure ethylic salt is prepared by heating camphoroxalic acid with highly dilute, absolute alcoholic hydrogen chloride. The compound crystallizes from ligroïn in long needles, aggregated into fern-like patterns, and melts at 40.5°. It is miscible with ether in all proportions, and does not form a copper salt. Its low melting-point has unfortunately hitherto prevented a determination of its crystallographic constants.

The ethylic salt readily combines with dry ammonia, in ethereal solution ; the compound is sparingly soluble in the ordinary media, darkens at about 200°, and melts at 225°. With hydroxylamine, at the ordinary temperature, the ethylic salt yields a compound which crystallizes in colorless, slender needles, melting at 120–121°. The yield is poor. With acetic anhydride ethylic camphoroxalate yields, as stated above, acetylcamphoroxalic acid. Bromine acts on ethylic camphoroxalate quite readily, forming first an additive compound, which gradually evolves hydrogen bromide ; the final product is oily, and resembles the bromocamphoroxalic acid described above.

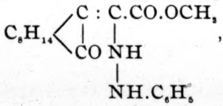
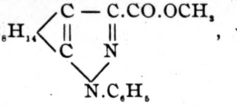
Attempts to obtain a benzoyl derivative of ethylic camphoroxalate by Schotten-Baumann's method, or by heating the substances together under varying conditions, were unsuccessful, nor were any better results obtained by the use of benzoic anhydride. These facts indicate that ethylic camphoroxalate is considerably more stable than the free acid, but, with only negative evidence, it would not be justifiable to go beyond this, and regard the ester as possessing a different constitution to that of the acid.

Methylic oxalate reacts with camphor, in presence of sodium, and yields *methylic camphoroxalate*,

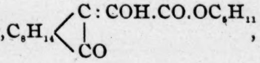


$$C_8H_{14}\left\langle \begin{array}{l} C : COH.CO.OCH_3 \\ | \\ CO \end{array} \right. .$$

The operation proceeds more slowly than with the homologue, apparently owing to the greatly inferior solubility of the intermediate sodium salt, which covers the sodium wire, and protects it from further action. The product closely resembles the ethylic ester in general properties. The pure compound is obtained by freezing the crude product, or by the etherification of camphoroxalic acid; it crystallizes in long arborescent needles, melts at 74.5°–75°, and is somewhat less readily soluble than the ethylic ester. Examination of the crystals showed that they belonged to the orthorhombic system.

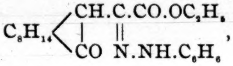
With phenylhydrazine, methylic camphoroxalate yields a *phenylhydrazide*,  , which crystallizes in slender colorless, needles melting at 204°–205°. When digested on the water-bath with glacial acetic acid, the phenylhydrazide is converted into *methylic camphylphenylpyrazolecarboxylate*,  , which crystallizes in colorless needles, and melts at 80.5°–81.5°. The nature of the compound is shown by its giving, when hydrolyzed, the camphylphenylpyrazolecarboxylic acid (m. p. 192°) described in the previous paper.

Isoamylic oxalate, prepared from purified fusel oil, readily combines with camphor in the presence of sodium. The reaction proceeds comparatively rapidly without extraneous heating, and the intermediate sodium compound is readily soluble in ligroïn. A comparison of the behavior of the three homologous oxalates towards camphor shows that the reactivity increases as the mass of the alkyl becomes greater, but this is by no means due to the effect of mass alone, the solubility in ligroïn or ether of the intermediate sodium salts is a most important factor, and this also increases with the mass of the alkyl, and therefore with its content of carbon.

Crude *isoamylic camphoroxalate*, 
$\mathrm{C_8H_{14}}\left<\begin{array}{l}\mathrm{C:COH.CO.OC_5H_{11}}\\ |\\ \mathrm{CO}\end{array}\right.$,
resembles the ethylic compound in general properties; on standing it gradually deposits needle-shaped crystals, which are comparatively sparingly soluble in ether and ligroïn, and melt at 98.5°–99.5°. Measurements indicate that the crystals belong to the triclinic system. A comparison of the crystallographic characters of camphoroxalic acid and of the methylic and isoamylic salts shows that the grade of symmetry of the crystals becomes lower as the molecular weight increases.

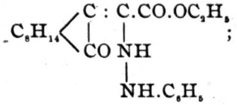
With phenylhydrazine, isoamylic camphoroxalate yields a crystalline, sparingly soluble *phenylhydrazide*.

The compound obtained by the interaction of ethylic camphoroxalate and phenylhydrazine, and described in the previous paper, was stated to be either a phenylhydrazone,



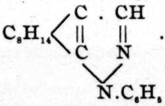
$$\mathrm{C_8H_{14}}\left<\begin{array}{ll}\mathrm{CH.}&\mathrm{C.CO.OC_2H_5}\\ |&\|\\ \mathrm{CO}&\mathrm{N.NH.C_6H_6}\end{array}\right.,$$

or a phenylhydrazide,



$$\mathrm{C_8H_{14}}\left<\begin{array}{ll}\mathrm{C}&\mathrm{:C.CO.OC_2H_5}\\ |&|\\ \mathrm{CO}&\mathrm{NH}\\ &|\\ &\mathrm{NH.C_6H_5}\end{array}\right.;$$

further investigation has shown that it has the latter constitution, as it is readily oxidized by heating with carefully purified mercuric oxide in presence of alcohol; the yield of oxidation-product was very poor.

Camphylphenylpyrazolecarboxylic acid when distilled over barium oxide yields an oily substance which gives Knorr's pyrazoline reaction. It probably contains camphylphenylpyrazole, . Sodium camphylpyrazolecarboxylate injected into the veins of dogs, is without any marked physiological action. Sodium camphoroxalate, under similar circumstances, is distinctly and rapidly toxic.

Experimental.

Action of Acetic Anhydride on Camphoroxalic Acid.

Camphoroxalic acid (1 molecule) readily dissolves in acetic anhydride (5 molecules) without perceptible evolution of heat; after boiling with a reflux-condenser for two hours, the liquid is poured into water, neutralized with sodium hydrogen carbonate, and the solid precipitate removed, dried, and recrystallized from a mixture of ether and ligroïn. It is deposited in clusters of colorless, slender needles, darkens at about 240°, and melts at 242°–242.5°. In alcoholic solution it gives no coloration with ferric chloride.

On repeating the experiment with another preparation of acetic anhydride, which, like the first, was from Kahlbaum, none of the above compound was produced, and a portion of the camphoroxalic acid was decomposed. Examination showed that the anhydride was impure; it was fractionated several times, finally over fused sodium acetate and phosphoric anhydride. A considerable number of experiments were made with this specimen of anhydride under varying conditions of temperature, with and without anhydrous sodium acetate and glacial acetic acid, but the yield of the new compound was always very small, and frequently none was formed. Two other substances were obtained in varying proportions. Both crystallize in colorless, slender needles, the one from ligroïn, the other from a mixture of chloroform and ligroïn; they melt at 190° and 133.5°–134.5°, respectively, the latter evolving gas. The former compound is insoluble in a solution of sodium hydrogen carbonate, but readily so in ether, and is produced by the action of benzoyl chloride on camphoroxalic acid. The second compound is also obtained by the action of acetic anhydride on ethylic camphoroxalate; after repeated recrystallization from a mixture of benzene and ligroïn it is deposited in reticulated, stellate, needle-shaped prisms. It is readily soluble in ether, benzene, chloroform, and glacial acetic acid, and is precipitated from the latter on dilution in an amorphous condition; sodium carbonate solution quickly dissolves it, and it gives no precipitate with calcium chloride in ammoniacal solution. Analyses gave the following results :

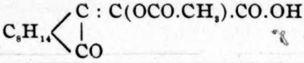
I. 0.29615 gram substance gave 0.1858 gram H_2O, and 0.6858 gram CO_2.

II. 0.2731 gram substance gave 0.1636 gram H_2O, and 0.63325 gram CO_2.

	Calculated for $C_{12}H_{15}O_4.CO.CH_3$.	Found. I.	II.
C	63.15	63.15	63.23
H	6.76	6.97	6.65

The first analysis was made with a specimen prepared from camphoroxalic acid ; the second with one from ethylic camphoroxalate.

The compound is therefore *acetylcamphoroxalic acid*,



$$C_8H_{14}\left\langle\begin{array}{l}C : C(OCO.CH_3).CO.OH \\ | \\ CO\end{array}\right. .$$

Very many attempts were made to devise a satisfactory method for the preparation of the compound, but without much success. When prepared from camphoroxalic acid, acetic anhydride alone should be used, and the mixture boiled in the manner described above ; the product is poured into water, neutralized with sodium hydrogen carbonate, and extracted with ether ; the aqueous solution is then treated with dilute sulphuric acid in excess, and extracted twice or thrice with ether. This ethereal solution is dried, the ether removed, and the residue allowed to crystallize spontaneously. To obtain the acetyl derivative from ethylic camphoroxalate, the crude ester (1 molecule) is mixed with acetic anhydride (2 molecules), diluted with three parts glacial acetic acid ; the solution is heated on the water-bath for fifteen minutes, then boiled for ten minutes, poured into water, and separated in the manner just described.

Action of Bromine on Acetylcamphoroxalic Acid.

The acetyl derivative reacts only slowly with bromine in chloroform solution at the ordinary temperature, but on warming hydrogen bromide is copiously evolved. After removal of the chloroform the residue showed no signs of crystallization, and was not further investigated. With bromine vapor at the ordinary temperature the well-dried acetyl derivative speedily reacts, and liquefies; hydrogen bromide is slowly evolved, but no crystalline product could be obtained.

Action of Bromine on Camphoroxalic Acid.

Bromine reacts with the acid more readily than with the acetyl derivative, but the results are similar. In chloroform solution the evolution of hydrogen bromide commences almost immediately after the addition of bromine, and without the application of heat. After removal of the chloroform the oily residue gave, in alcoholic solution, a reddish-green coloration with ferric chloride. In order to eliminate, if possible, any secondary action of hydrogen bromide, the behavior of silver camphoroxalate towards bromine was examined, but only oily products could be obtained. Liquefaction speedily takes place when camphoroxalic acid is exposed to bromine vapor at the ordinary temperature, and hydrogen bromide is slowly evolved; the oil was dissolved in ether, the solution washed with sodium carbonate solution, and the alkaline liquid acidified with dilute sulphuric acid, and extracted with ether. This ethereal solution is reddish-brown, and leaves a similarly colored oily residue when evaporated at the ordinary temperature, but if the ether is distilled off on the water-bath, an almost colorless oil is obtained which, in alcoholic solution, gives no coloration with ferric chloride. After remaining for a week, hard crystalline nodules are deposited, which melt at about 130°, but could not be purified by crystallization. The substance is readily soluble in chloroform or ether at the ordinary temperature, but when the solutions are evaporated spontaneously, or by means of a rapid current of air, oil is always found with the crystals.

The analytical results show that the compound consisted of bromocamphoroxalic acid, $C_{12}H_{15}O_4Br$ (91.7 per cent.), and oxalic acid (8.3 per cent.); the latter could not be removed owing to the difficulties described above. The bromo-acid has well-developed acidic properties, and readily dissolves in sodium carbonate solution with evolution of carbonic anhydride; in alcoholic solution ferric chloride produces a reddish-brown precipitate. The *silver salt* is colorless and slowly decomposes, silver bromide being produced. The *copper salt* is pale blue, and tolerably readily soluble in water, from which it can be recrystallized; it melts at about 65°.

When reduced with zinc dust and acetic acid the bromo derivative yields only oily products, but by the action of magnesium amalgam, prepared by H. Fleck's method,[1] at the ordinary temperature, in absolute alcoholic solution, the bromine is easily removed. The resulting product is similar to camphoroxalic acid in general properties, but melts at 84°–84.5° instead of at 88°.

The crystals appear to be monoclinic,[2] and consist of six-sided plates. They are faintly doubly refracting, and, on the large face (001), show the triaxial interference-figure. Optical character +. The axial plane is nearly perpendicular to (001). The plates are generally aggregates, and the angles are not measurable with a reflecting goniometer. With the microscope goniometer the angles of the plates are about 120°.

Action of Barium Hydroxide on Camphoroxalic Acid.

The acid was intimately mixed with the hydroxide in equimolecular proportion, dried at 100°, and distilled in a current of purified, well-dried hydrogen. The distillate had a peculiar, pungent, characteristic odor, but from it only water and camphor could be isolated. The residue also contained a little camphor, together with barium oxalate, showing that the camphoroxalic acid had been hydrolyzed at the position of the double linkage.

Action of Heat on Camphoroxalic Acid.

Attempts to obtain an isomeric compound by heating camphoroxalic acid were unsuccessful. No change is produced in its melting-point by prolonged heating at 150°; at 190°–200° a little carbonic anhydride is evolved, but the greater portion is unchanged even at the end of six hours. Another portion was heated at 250° until gas evolution ceased, and the oily residue was distilled under the ordinary pressure. The product consisted mainly of unchanged acid, together with camphor, showing that a portion of the original acid had been hydrolyzed.

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[1] Ann. Chem. (Liebig), (1892) **276**, 129; J. Am. Chem. Soc., **17**, 1895, 789.

[2] I am indebted to Dr. A. P. Brown, of the University of Pennsylvania, for all the crystallographic data in this paper.

Action of Benzoyl Chloride on Camphoroxalic Acid.

Heat is absorbed when benzoyl chloride (1.5 molecules) is mixed with camphoroxalic acid (1 molecule); when heated the mixture evolves hydrogen chloride and darkens slightly; after fifteen minutes it was poured into water, treated with sodium hydrogen carbonate, and extracted with ether in the manner described in the experiments with acetic anhydride. The alkaline extract yielded, in very small quantity, a compound melting at 192°–193°; it is insoluble in ligroïn, sparingly so in alcohol, and readily in chloroform; it gives no coloration, in alcoholic solution, with ferric chloride, and appears to be an anhydride identical with one of the products of the action of acetic anhydride on camphoroxalic acid (see above). From the acid ethereal extract only benzoic acid, and occasionally a little unchanged camphoroxalic acid could be obtained.

Action of Benzoic Anhydride on Camphoroxalic Acid.

No definite product could be obtained by the action of benzoic anhydride on camphoroxalic acid; at about 110° crystals of benzoic acid sublimed, and at 150° carbonic anhydride was evolved; the heating was continued at this temperature until no more gas came off, the residue then poured into water, treated with sodium hydrogen carbonate, and extracted with ether in the manner already described. The alkaline ethereal extract gave only a very small residue, which did not become colored when dissolved in alcohol and treated with ferric chloride. From the acid ethereal extract only benzoic acid could be isolated.

Action of Phenylhydrazine on Camphoroxalic Acid.

The substances, in equimolecular proportions, are separately dissolved in anhydrous ether free from alcohol, the solutions mixed, and heated on the water-bath during two hours with a reflux-condenser. The yield is good. The product is deposited from alcohol, on the addition of ether, in minute colorless needles which darken at 205°, and melt and evolve gas at 214°–215°. It is readily soluble in alcohol (95 per cent.), sparingly so in ether and ligroïn, and insoluble in water. Phenylhydrazine is regenerated by the action of soda or dilute mineral acids. When boiled with water a gas, apparently nitrogen, is evolved. In alcoholic solution it gives a red coloration with ferric chloride, whilst a dark purple one is produced with concentrated nitric acid. The above reactions indicate that the compound is *phenylhydrazine camphoroxalate.*

Action of Dilute Hydrochloric Acid and of Dilute Sulphuric Acid on Camphoroxalic Acid.

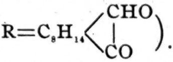
Camphoroxalic acid (5 grams) is heated in a sealed tube during eight hours, at 135°, with concentrated hydrochloric acid (6 cc.), and water (12 cc.); on cooling there is no pressure in the tube, and the contents consist of a slightly colored liquid with a hard, brittle, yellowish-brown, horny solid, covered with white arborescent crystals. This is dried, extracted several times with ligroïn to remove unchanged camphoroxalic acid, and crystallized from benzene once or twice. It is deposited in clusters of colorless needles, melting at 92°–93°. It gives, in alcoholic solution, a deep-blue coloration with ferric chloride. It is readily soluble in chloroform, from which it may be recrystallized by the addition of ligroïn. The compound is sparingly soluble in water, dilute hydrochloric acid, or ligroïn, readily dissolves in soda, ammonia, and sodium carbonate solution at the ordinary temperature. No sparingly soluble salts could be prepared. This property affords a ready means of proving that any specimen is free from oxalic acid or camphoroxalic acid since both these give a white precipitate on the addition of calcium chloride in presence of ammonia. The use of dilute sulphuric acid in place of hydrochloric acid is preferable in some respects, the conditions being: camphoroxalic acid (5 grams), dilute (1 : 3) sulphuric acid (24 cc.), heated at 135°–150°, during seven hours. After the extraction with ligroïn it is sometimes advantageous to dissolve the residue in excess of baryta water, treat the solution with carbonic anhydride until barium carbonate ceases to be precipitated, filter, acidify, and extract the liquid with ether several times. If the proportion of dilute sulphuric acid is increased to 16 cc. per gram of camphoroxalic acid, the mixture being heated in the manner described above, a portion of the latter is hydrolyzed to oxalic acid and camphor.

Analyses gave the following results:

I. 0.2523 gram substance gave 0.1769 gram H_2O, and 0.5148 gram CO_2.

II. 0.32725 gram substance gave 0.2231 gram H_2O, and 0.66695 gram CO_2.

	Calculated for $C_{12}H_{20}O_6$.	Found.	
		I.	II.
C	55.38	55.64	55.58
H	7.69	7.79	7.57

These results agree with an additive compound of camphoroxalic acid and $2H_2O$. The constitution of the substance has not yet been determined. It may be mentioned in this connection that Bishop, Claisen, and Sinclair[1] describe some ferric salts of formyl camphor which exist only in solution, and vary in color from blue to green; their composition is expressed by the formulæ $FeRCl_2$ and FeR_2Cl  $\left(R=C_8H_{14}\left\langle\begin{matrix}CHO\\ |\\ CO\end{matrix}\right.\right)$. The dark-red color produced by mixing ferric chloride with an alcoholic solution of camphoroxalic acid or of ethylic camphoroxalate, does not change when the reagent is added in large excess.

Crystallographic Properties of Camphoroxalic Acid.

The substance crystallizes in short prisms $(10\bar{1}0)$ terminated by the basal pinacoid (0001) belonging to the hexagonal system. No other forms were observed, and no axial ratio could be determined. The crystals give the uniaxial interference figure on (0001); optical character +. They exhibit rotatory polarization; one specimen revolved the plane of polarization 10° to the right for a thickness of 0.65 mm. Some of the hexagonal plates appear to show right and left rotatory polarization in different sectors.

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[1] Ann. Chem. (Liebig), (1895) **281**, 343.

Preparation of Pure Ethylic Camphoroxalate.

Camphoroxalic acid (22.4 grams) is dissolved in absolute alcohol (120cc.), containing hydrogen chloride (5.52 grams), and boiled during six hours in a reflux-apparatus. The alcohol is distilled off on the water-bath, the residue poured into water, neutralized with sodium hydrogen carbonate, and extracted twice with ether. The ethereal solution is dried and distilled; the oily residue solidifies after remaining for some time, or more quickly when cooled. The ethereal salt is deposited from ligroïn in fern-like aggregates consisting of long needles, melting at 40.5°. It is miscible with ether in all proportions, and is extremely readily soluble in the ordinary media. No copper salt could be isolated; when mixed, in alcoholic solution, with cupric acetate, or in ethereal solution with ammoniacal cupric acetate, the color changes from blue to green, but on evaporating the liquid only resinous products were deposited.

The yield is 72.3 per cent. of the theoretical, but if the acid recovered from the alkaline aqueous liquid is deducted, the yield is quantitative. The above description of the pure ester shows how closely its properties resemble those of the impure product of which an account was given in the previous papers, and indicates that the specimens of the latter cannot have contained much ethylic oxalate.

Analysis gave the following results:

0.2401 gram substance gave 0.1584 gram H_2O, and 0.5854 gram CO_2.

	Calculated for $C_{14}H_{20}O_4$.	Found.
C	66.66	66.49
H	7.93	7.33

In order to test the question of the homogeneity of camphoroxalic acid, a quantity was etherified to the extent of about 50 per cent.; the remainder proved to be identical with the specimens prepared in the ordinary manner. Measurements of the crystals of ethylic camphoroxalate have not been made, owing to their low melting-point; they tend to loose their individuality soon after they have been prepared.

Action of Ammonia on Ethylic Camphoroxalate.

Carefully dried ammonia produces a white precipitate with ethylic camphoroxalate dissolved in anhydrous ether, free from alcohol. The compound is very sparingly soluble in the ordinary media, and was purified by washing with ether; it darkens at about 200°, and melts at 225°. It gives no coloration with alcohol and ferric chloride, or with concentrated nitric acid, in which it dissolves comparatively slowly. At the ordinary temperature dilute sulphuric acid or soda decomposes it slowly; when heated the action is more rapid, and the components are regenerated. If heated alone, ammonia is evolved, a white sublimate is deposited, and a carbonaceous residue is left.

Action of Hydroxylamine with Ethyl Camphoroxalate.

The ethylic salt (1 molecule) is dissolved in alcohol and mixed with a concentrated aqueous solution of hydroxylamine hydrochloride (3.5 molecules); alcohol is added, if necessary, to obtain a clear solution, which is then rendered faintly alkaline with sodium hydrogen carbonate. A white granular precipitate is gradually formed. After remaining at the ordinary temperature during six days, the liquid is poured into water, acidified with dilute sulphuric acid, and extracted three times with ether. The ethereal solution is dried and distilled, and the residue recrystallized twice from a mixture of toluene and ligroïn; it is deposited in colorless, slender needles, melting at 120°-121°. The compound is readily soluble in caustic soda, more slowly in sodium carbonate solution. It dissolves in dilute sulphuric acid when heated, but crystallizes out on cooling. Water does not dissolve it, but when heated it melts and floats on the surface. The nature of the compound is at present uncertain, possibly it may prove to be an additive compound similar to that formed by camphoroxalic acid, which melts at 146.5°, and was described in the previous paper.

Action of Acetic Anhydride on Ethylic Camphoroxalate.

Ethylic camphoroxalate (1 molecule) is mixed with acetic anhydride (2 molecules), diluted with glacial acetic acid

(3 parts), and the liquid heated on the water-bath during fifteen minutes, then boiled during ten minutes. The product is poured into water, and treated in the manner described in the experiments with acetic anhydride and camphoroxalic acid. The only product which could be isolated is the acetylcamphoroxalic acid (m. p. 133.5°–134.5°) described on page 324. The yield is rather poor, and numerous variations were made in the experimental conditions in order to improve it, or to prepare some other compound, but without success.

Action of Bromine on Ethylic Camphoroxalate.

The behavior of ethylic camphoroxalate towards bromine resembles that of the free acid; in chloroform solution the addition of bromine to the ester is attended with evolution of heat, but the color of the bromine is only slowly discharged. When the liquid is heated hydrogen bromide is copiously evolved. After spontaneous evaporation of the chloroform a yellowish oil remains which has a characteristic penetrating odor, and slowly deposits crystals of oxalic acid. By the action of bromine vapor in the manner described in the experiments with camphoroxalic acid, an oily compound is formed which could not be induced to crystallize. Its color is at first red, but as evolution of hydrogen bromide proceeds it gradually becomes faintly yellow.

Action of Benzoyl Chloride and of Benzoic Anhydride on Ethylic Camphoroxalate.

All attempts to obtain a benzoyl derivative of ethylic camphoroxalate were unsuccessful; when treated by Schotten-Baumann's method benzoic acid was the only product that could be isolated, and a similar result was obtained by heating the substances mixed in various proportions, and during different periods. In every case the ethylic salt was either recovered unchanged, or it suffered decomposition. The results were similar when benzoic anhydride was employed in place of the chloride, although the substances were heated at 150° during four hours. In these circumstances almost all the ethylic salt was recovered.

The details of the experiments are similar to those given in the case of camphoroxalic acid and benzoyl chloride or benzoic anhydride.

The greater relative stability of the ethylic salt towards these reagents in comparison with the acid is somewhat striking.

Action of Methylic Oxalate on Camphor.

Camphor (31.5 grams = 1.5 molecules) and methylic oxalate (17.7 grams = 1 molecule) are mixed with ligroïn (500 cc.), which has been carefully dried over sodium, and sodium wire (3.5 grams = 1 atom) is added ; the reaction takes place slowly, and in order to render it approximately complete the ligroïn must be boiled on the water-bath with a reflux-apparatus during two to three hours. Methylic oxalate is only sparingly soluble in ligroïn, and the same applies to the sodium derivative, consequently some metallic sodium is always unattacked, and care is required in treating the product with water. The methylic camphoroxalate is separated from camphoroxalic acid exactly like ethylic camphoroxalate in the manner described in the previous paper. The total yield of acid and methylic salt is 40–45 per cent. of the theoretical, but the relative amounts vary greatly according to the duration of the heating ; if this is prolonged the proportion of acid increases considerably. In one experiment the ratio, ester : acid = 1 : 0.74, in another, when the heating was continued during nearly five hours, the ratio was 1 : 2.1.

The acid was found to be identical with that obtained by the interaction of ethyl oxalate and camphor.

In general properties methylic camphoroxalate closely resembles the ethylic salt. In alcoholic solution it gives a deep-red coloration with ferric chloride, and occasionally the crude product crystallizes.

Pure methylic camphoroxalate is readily obtained by boiling the acid (22 grams) with methylic alcohol (120 cc.), containing 4.25 per cent. by weight of hydrogen chloride. The heating is continued during six hours, and the product treated in the manner described for the preparation of pure ethylic camphoroxalate. The methylic salt is readily soluble

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in alcohol and ether, and crystallizes from ligroïn in long arborescent needles melting at 74.5°–75°.

Analyses gave the following results:

I. 0.2511 gram substance gave 0.1605 gram H_2O, and and 0.60415 gram CO_2.

II. 0.3029 gram substance gave 0.2045 gram H_2O.

	Calculated for $C_{13}H_{18}O_4$.	Found. I.	II.
C	65.54	65.61	....
H	7.56	7.10	7.50

The crystals belong to the orthorhombic system. The faces are somewhat curved or irregular rendering measurements difficult. The forms observed were the pyramid (111), prism (110), and brachypinacoid (010). Angles:

$$110 \wedge 110 = 87^\circ 12'$$
$$110 \wedge 111 = 50^\circ 44' 30''$$
$$110 \wedge 010 = 46^\circ 24'$$

Axial ratios $\breve{a} : \bar{b} : \acute{c} = 0.9523 : 1 : 0.5649$. The extinction observed on (110) and (010) was parallel to $\acute{c}$.

Action of Phenylhydrazine on Methylic Camphoroxalate.

Methylic camphoroxalate (22.7 grams = 1 molecule) is dissolved in carefully dried ligroïn (250 cc.); phenylhydrazine (10.8 grams = 1.25 molecules) added, and the mixture heated on the water-bath with a reflux-apparatus during two and a half hours. The solid product is separated, well washed with dry ether, and recrystallized twice from methylic alcohol. It forms slender white needles, melts at 204°–205°, is insoluble in ligroïn, very sparingly so in chloroform, benzene, or ether, but dissolves more readily in ethylic or methylic alcohol, and in ethylic acetate. Concentrated nitric acid produces a blue coloration which appears purple by transmitted light; it gradually changes to brown, and finally becomes light red. Addition of water to the recently prepared nitric acid solution causes the compound to be reprecipitated. Concentrated sulphuric acid produces no coloration at the ordinary temperature even on the addition of a crystal of potassium bichromate; when heated, gas is evolved. The compound dissolves in dilute sulphuric acid, and in acetic acid when heated, but is insoluble in hot sodium hydrate solution. It is stable when purified, but the crude substance readily decomposes. Analyses gave the following results :

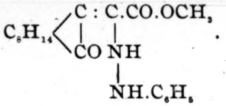
I. 0.3498 gram substance gave 0.2305 gram H_2O, and 0.88315 gram CO_2.

II. 0.38295 gram substance gave 0.2564 gram H_2O, and 0.9742 gram CO_2.

III. 0.2719 gram substance gave 22 cc. nitrogen at 25.5° and 765 mm.

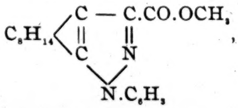
	Calculated for $C_{19}H_{24}N_2O_3$.	Found. I.	II.	III.
C	69.51	68.86	69.38	....
H	7.31	7.32	7.43	....
N	8.53	....	....	9.08

From its properties, mode of preparation, and analogy with the corresponding compound of ethylic camphoroxalate (see under) the compound is a *phenylhydrazide*,



The analysis requires some care, otherwise carbon monoxide is produced, and a portion escapes oxidation.

When mixed with glacial acetic acid, and gently evaporated to dryness on the water-bath, the phenylhydrazide yields *methylic camphylphenylpyrazolecarboxylate*,



which is deposited from ligroïn in colorless needles, melting at 80.5°–81.5°. The compound was identified by hydrolyzing it with potash; when acidified, the solution precipitates the camphylphenylpyrazolecarboxylic acid described in the previous paper; it melts at 193°–194°, not at 102° as stated there.

Action of Isoamylic Oxalate on Camphor.

The only method mentioned in Beilstein's "Handbuch" for the preparation of isoamylic oxalate is one employed by Friedel and Crafts, which consists in heating ethylic oxalate with isoamyl alcohol at 220°–250°; in addition to isoamylic oxalate, ethylic alcohol, diethylic ether, carbon monoxide, and carbon dioxide are produced. Such a method is obviously not well adapted to the preparation of isoamylic oxalate in quantity, consequently it was obtained in the following manner:[1] Isoamylic alcohol (193 grams), obtained by the fractionation of the fusel oil, is mixed with dehydrated oxalic acid (101 grams), and digested on the water-bath during six hours. The upper layer of liquid is removed and fractionated under the ordinary pressure, the portion boiling at 255°–265° being retained; most of it boiled at 262°—the true boiling-point according to R. Schiff. The yield is 150 grams = 58 per cent. of the theoretical. Isoamylic camphoroxalate is prepared by dissolving camphor (31.5 grams = 1.5 molecules), in anhydrous ligroïn (500 cc.), adding isoamylic oxalate (34.5 grams = 1 molecule), and sodium wire (3.5 grams = 1 atom). The reaction commences vigorously, and proceeds without the aid of heat until about half the sodium is dissolved. The sodium salt is readily soluble in ligroïn. The subsequent operations were performed in the manner described in the previous paper except that the acidified aqueous solution was extracted with ether more frequently, as the isoamylic ester is less soluble than the lower homologues. The yield is 12.5 grams of crude ester and 10.7 grams of crude camphoroxalic acid = 28.4 and 31.8 per cent. of the theoretical, respectively. The ratio, ester : acid = 1 : 1.12. The comparatively large yield of acid is probably due to incomplete separation of the ester from the borneol. This is a matter of some difficulty for the reason stated above. The influence of the various alkyl groups on the reaction is clearly marked; it proceeds more readily as the molecular weight of the alkyl increases; whilst this may arise in part from the greater mass, the chief factor influencing the result is undoubtedly the greater solubility in ligroïn of the intermediate sodium salt, which increases as the content of carbon rises.

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[1] I am indebted to Dr. Fleck, of the University of Pennsylvania, for suggesting the method and for supplying me with specimens of the ester.

The crude isoamylic ester gives, in alcoholic solution, a red coloration with ferric chloride, and slowly deposits needle-shaped crystals; these are insoluble in benzene or ligroïn, and only sparingly so in chloroform and ether; they melt at 98.5°–99.5°.

A crystallographic examination showed that the crystals examined were dull, and some of the faces did not give images. Measurements indicate that they are triclinic. The forms measured were assumed as the three pinacoids; a prism which occurred gave no satisfactory image, and therefore the axial ratios of $\breve{a} : \bar{b}$ could not be determined. Angles:

$$001 \wedge 010 = 107^\circ 26'$$
$$001 \wedge 100 = 86^\circ$$
$$100 \wedge 010 = 76^\circ 36'.$$

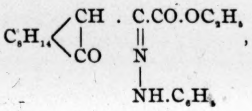
This gives by calculation $\alpha = 108^\circ\ 59'\ 30''$; $\beta = 81^\circ\ 22'$; $\gamma = 74^\circ\ 36'$.

Examined in polarized light the crystals are triaxial and strongly doubly refracting. The index of refraction is moderate.

Isoamylic camphoroxalate readily combines with phenylhydrazine, heat being evolved. The product is very sparingly soluble in the ordinary media; it dissolves in isoamylic alcohol, and is reprecipitated on the addition of ether, but at the temperature of the boiling alcohol a portion of the substance suffers decomposition so that its more complete examination has not yet been made.

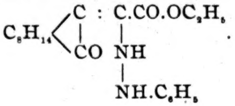
Oxidation of Ethylic Camphoroxalate Phenylhydrazide.

The compound produced by the interaction of ethylic camphoroxalate and phenylhydrazine was stated, in the previous paper, to be either a phenylhydrazone,



$$C_8H_{14}\left\langle\begin{array}{l}CH\\ |\\ CO\end{array}\right.\begin{array}{l}.\ C.CO.OC_2H_5\\ \quad\ \|\\ \quad\ N\\ \quad\ |\\ \quad\ NH.C_6H_5\end{array},$$

or a phenylhydrazide,

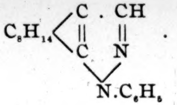


$$C_8H_{14}\left\langle\begin{array}{l}C\\ |\\ CO\end{array}\right.\begin{array}{l}:\ C.CO.OC_2H_5\\ \quad |\\ \quad NH\\ \quad |\\ \quad NH.C_6H_5\end{array}.$$

The following experiments show that the latter surmise is correct. Precipitated mercuric oxide, carefully washed free from alkali, and dehydrated by means of absolute alcohol in the manner described by Nef, is added to the phenylhydrazide, suspended in absolute alcohol, and the mixture is heated on the water-bath. Reaction commences immediately, the oxide becomes gray, and more is added as required. When no further change is perceptible the greater portion of the alcohol is distilled off, the residue poured into water, and extracted with ether; after drying the solution and removing the ether, a fluorescent, somewhat tarry residue is obtained which is permeated with crystals. The latter consist partly of unchanged phenylhydrazide, partly of a compound crystallizing in colorless monoclinic plates resembling copper sulphate in shape, and melting at 112.° The quantity of this substance was only small. The purification of the products of the reaction is a matter of considerable difficulty, as decomposition readily takes place.

Action of Barium Oxide on Camphylphenylpyrazolecarboxylic Acid.

The acid (1 molecule) is intimately mixed with barium hydroxide (1.5 molecules), dried at 100° in an atmosphere free from carbon dioxide, mixed with finely-divided iron to increase its conductivity, and distilled under a pressure of about 50 mm. The distillate consists of a yellowish-green oil which showed no tendency to crystallize. It gave a slight reddish-brown color, in alcoholic solution, with ferric chloride, and a deep reddish-purple one with concentrated nitric acid. It gives Knorr's pyrazoline reaction, and therefore presumably contains camphylphenylpyrazole,



Camphylisoxazole.

Before the preparation of camphylisoxazole, described in the previous paper, the following experiment was performed in order, if possible, to induce the carbonyl group of the camphor molecule to react with hydroxylamine. The hydroxylamine addition-product of camphoroxalic acid was dissolved in glacial acetic acid, hydroxylamine hydrochloride (4 molecules) added, and the mixture heated on the water-bath during six hours. The cold solution deposited crystals resembling those of potassium nitrate in appearance. The product of the reaction was poured into water, neutralized with sodium hydrogen carbonate, made slightly acid with dilute sulphuric acid, and extracted with ether three times. The ethereal solution was dried, and the ether removed; the residue, after purification, proved to be camphylisoxazole.

Physiological Action of Sodium Camphylphenylpyrazolecarboxylate.[1]

The experiments were made on dogs, the salt being administered in doses of 0.8 gram per kilo of body weight, by intravenous injection of a 5 per cent. solution in "normal saline solution" (containing 0.75 per cent. of sodium chloride). Successive injections were made of 5, 10, and 15 cc.; immediately following the last injection a slight fall of blood pressure occurred, followed by a gradual rise to normal. A further injection of 5 cc. caused a slight fall in blood pressure, but it rose almost to normal in less than seven minutes. At this stage the reflexes are well given, and the pupil is dilated. A further injection of 5 cc. produced a more pronounced and steady fall of pressure, accompanied by slight struggling movements; the knee-jerk is absent but the corneal reflex is given well; the pupil is dilated. The respirations became feeble and ceased, the last one taking place about four and a half minutes after the final injection. The temperature two and a half minutes after the last injection was 38.1°, and the blood pressure only a few mm. The following table gives the experimental details: Weight of dog 7.95 kilos. Normal temperature 39.6°.

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[1] I am indebted to Dr. Carter, Professor of Physiology in the University of Texas, for the experimental data on which this description and that of the action of sodium camphoroxalate are based.

Time.	Blood pressure in mm.	Pulse beat in ten seconds.	Respiration rate in thirty seconds.	Remarks.
4.56.20	79	28	15	5 cc. injected.
4.57.10	82	28	17	10 cc. injected.
4.58.00	67	27	18	
5.00.10	79	28	27	15 cc. injected.
5.00.30	51	26	27	
5.02.20	51	24	32	
5.03.30	56	23	18	
5.09.00	67	23	15	
5.10.00	73	21	..	Respiration unchanged.
5.15.00	76	29	42	
5.15.30	79	..	..	5 cc. injected.
5.15.50	56	..	..	
5.16.20	56	..	..	Reflexes good, pupil dilated.
5.22.20	67	25	28	5 cc. injected.
5.23.00	38	18	18	Slight struggling.
5.23.20	32	17	..	No knee-jerk, corneal reflex good, pupil dilated.
5.24.00	22	15	30	Respiration very shallow.
5.25.00	13	..	..	Temp. 38.1°.

Physiological Action of Sodium Camphoroxalate.

An experiment was conducted in a similar manner to that with the pyrazolecarboxylate. The salt is rapidly toxic. It was administered by intravenous injection of a 2 per cent. solution in "normal saline"; 3 cc. of this solution, introduced into the jugular vein of a dog, caused almost immediate arrest of respiration and simultaneous fall of blood pressure. Seventy-five seconds after the injection the blood pressure had fallen from 133 mm. to 56 mm., and 2 seconds later the heart collapsed, from this point only beating at irregular intervals till death took place. It is evident that the salt acts powerfully on the respiratory center, but the rapid fall in blood pressure indicates that death is not entirely due to asphyxia, the vaso-motor center being also paralyzed.

The following table contains a summary of the experimental results :

Weight of dog 7.03 kilos. Two per cent. solution of sodium camphoroxalate, in "normal saline" solution, injected into the jugular vein.

Time.	Blood pressure in mm.	Remarks.
2.46.25	133	
2.46.45		3 cc. injected.
2.47.05	120	Respiration arrested.
2.47.40	56	
2.47.42	16	Heart collapsed. Feeble beats occurred at irregular intervals for about forty seconds.

This investigation is being continued and extended in various directions.

I desire to avail myself of this opportunity of expressing my deep obligations and cordial thanks to Professor Edgar F. Smith, of the University of Pennsylvania, both for his liberality in allowing this investigation to be conducted in the John Harrison Chemical Laboratory, and for his kindly encouragement and advice during its progress.

LEWIS INSTITUTE, CHICAGO, ILL.

REVIEWS.

THE ARRANGEMENT OF ATOMS IN SPACE. BY J. H. VAN 'T HOFF. Second revised and enlarged edition, with a preface by JOHANNES WISLICENUS, Professor of Chemistry at the University of Leipzig, and an appendix on Stereochemistry among Inorganic Substances by ALFRED WERNER, Professor of Chemistry at the University of Zürich. Translated and edited by ARNOLD EILOART. Longmans, Green & Co., London, New York, and Bombay. 1898. viii + 211 pp.

This, as the title-page implies, is a translation of the second edition of van 't Hoff's book of the same title that appeared in 1894, and the latter in turn was a freely revised version of the book that appeared in 1877, when the fundamental theory of stereochemistry was first given to the world in a satisfactory form. It is unnecessary to go into details in discussing this book. The translator has for some time been occupied with the literature of stereochemistry and has a very thorough knowledge of the subject. He is therefore unusually well qualified for the work of translation, and the work appears to have been well done. Anyone who wishes to consult a book by a master summing up the results obtained in the field of stereochemistry will do well to get this book.

In the Appendix, prepared by Werner, the ideas which were first worked out by him bearing upon the subject of stereochemical isomerism of inorganic compounds are briefly presented—too briefly for the purpose, as without a careful study of a number of examples as presented in Werner's original articles it is very difficult for anyone to get a clear idea of his theory. I. R.

TABELLARISCHE UEBERSICHT DER MINERALIEN NACH IHREN KRYSTALLOGRAPHISCHCHEMISCHEN BEZIEHUNGEN GEORDNET. VON P. GROTH. Vierte Vollständig Neu Bearbeitete Auflage. Brauschweig: Vieweg. 1898. viii + 184 pp.

This admirable book appeals to the chemist more strongly than most books on mineralogy, as it is evident that the author has some appreciation and understanding of the chemistry of the present time, and he has endeavored in a sensible way to utilize his knowledge for the purpose of simplifying the presentation of the mass of material that the mineralogist has to deal with. While the author's interest in the subject of chemical constitution leads him to raise the question in each group and in connection with each species as to the chemical constitution of the class and of the individual, a cautious chemist will perhaps in some cases be a little surprised to find with what confidence Professor Groth presents the formulas. While a cautious chemist is not likely to be misled by these symbols, a mineralogist without the proper chemical training will be apt to accept them as final and thus be led to assume that more is known regarding the chemistry of the substances represented than is actually the case. On the whole, however, it is better for the mineralogist to accustom himself to these constitutional formulas than to continue to use the old electrochemical formulas that are so commonly used in books on mineralogy.

As regards the changes in the treatment of the subject of the chemical constitution of minerals the author says: "The views upon this subject have been cleared up in many points since the appearance of the third edition in consequence of many new investigations, among which should be prominently mentioned the numerous mineral analyses of Penfield and his students as well as the comprehensive theoretical articles by Clarke." I. R.

PRACTICAL TOXICOLOGY FOR PHYSICIANS AND STUDENTS. By Prof. Dr. RUDOLF KOBERT. Translated and edited by L. H. FRIEDBURG, Ph.D. New York: William R. Jenkins. 1897. 201 pp.

This book has come into extensive use in Germany, and has proved of service in other countries. It, therefore, appears probable that it will be found of value to American students. The translator has used the book with his students for several years, and is hence perfectly familiar with it. It is far from pretentious, and is not "intended to compete with the existing handbooks of toxicology." To use the author's own words: "The aim of the book shall be reached if it can be used to advantage by such physicians and students of medicine, who are not able to spend much time or much money upon the study of toxicology."

THE KEKULÉ MONUMENT.

The attention of the readers of this Journal is specially asked for the circular accompanying this number. It explains itself fully, and it is hoped that many will respond. There is scarcely any chemist who has exerted an influence equal to that exerted by Kekulé upon the advance of chemistry during the past thirty years. It is difficult to realize how thoroughly the chemistry of to-day is saturated with his ideas. Not only do we owe to him the wonderfully fruitful benzene theory, but we owe to him very largely our present conceptions of the constitution of chemical compounds—conceptions which, however imperfect they may be, have been and are of the greatest service to all chemists, whether they are working with organic or with inorganic compounds, on problems of constitution or of dynamics, in the field of pure chemistry or of chemical industry.

Any subscriptions to the Kekulé fund sent to this Journal will be acknowledged and forwarded to the General Treasurer in Germany.

I. R.

Correction.

Vol. **20**, pages 131 and 132: *For* "Pren" *read* "Preu."